Influence of surfactant concentration on nanohydroxyapatite growth

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Abstract. Nanohydroxyapatite particles with different morphologies were synthesized through a microwave coupled hydrothermal method using CTAB as a template. A successful synthesis of nanosized HAP spheres, rods and fibres is achieved through this method by controlling the concentration of the surfactant. The concentration of the surfactant was tuned in such a way that the desired HAP nanostructures were obtained. The resultant powders were sintered at 900 °C in order to obtain phase pure HAP particles. The results obtained by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques have substantiated the formation of nanosized HAP spheres and fibres.

Keywords. Biomedical applications; hydroxyapatite; microwave processing; calcination; X-ray methods.

1. Introduction

Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAp], the prime constituent of bone and teeth has attracted a great deal of attention in biomedical applications owing to its close similarity in chemical composition with the mineral part of natural bone and teeth (Hench 1991; Rambo *et al* 2006; Kalita *et al* 2007). Recently, main interest is not only controlling the stoichiometry of synthetic HAp, but also to control the shape, size and agglomeration characteristics of their particles (Walsh and Mann 1996; Sarda *et al* 1999). It has been shown that many clinical applications of HAp mainly depend on shape, morphology and size of HAp particles (Suchanek and Yoshimura 1998). Hence, it is possible to enhance the biological performance of hydroxyapatite by controlling the morphology, particle size and distribution. Therefore, a number of processing routes have been developed for preparing hydroxyapatite powders, including sol–gel (Bezzi *et al* 2003; Anee Kuriakose *et al* 2004), hydrothermal (Hattori and Iwade 1990; Remant Bahadur *et al* 2008), microemulsion (Murray *et al* 1995; Lim *et al* 1996) and mechanochemical (Kim *et al* 2000; Yeong B *et al* 2001) methods. Recently, we have reported the synthesis of nanohydroxyapatite particles by an ultrasonic coupled sol–gel method (Gopi *et al* 2008).

Eventhough these methods have been used to fabricate nanosized HAp, there are intensive interests to find gentle and rapid ways for the synthesis of pure hydroxyapatite nanoparticles. Mass production of high purity hydroxyapatite is reported via time-consuming and tedious processes

only (Lerner *et al* 1991). Microwave irradiation is an efficient method which solves this problem and provides rapid, facile and convenient synthesis procedures (Lerner *et al* 1991; Macipe *et al* 1998; Sarig and Kahana 2002; Liu *et al* 2005; Rameshbabu *et al* 2005). Hence, microwave heating has been employed instead of conventional heating to synthesize nanosized hydroxyapatite particles owing to its unique heating features and precipitation of nanosized HAp using microwave irradiation has also been reported (Arami *et al* 2009). Microwave irradiation can be successfully used for synthesizing various nanostructured materials due to its unique properties and is increasing the yield of precipitations (Jiang *et al* 2006; Yang *et al* 2007).

Although control over microstructure seems to be a big challenge with traditional methods, it is known that the controlled nucleation and crystal growth process mediated by macromolecular control would finally result in uniform and fine-shaped products. Traditional clinical applications of calcium phosphates have mainly focused on highly crystalline ceramics (Liu *et al* 2002). Therefore, it is important to synthesize HAp nanofibres for biomedical applications. Previous studies have shown that nanofibres affect the cellular behaviour by the way of promoting proliferation and differentiation of cells. This phenomenon occurs because, the cells attach and organize around the fibres with diameters smaller than that of cells and hence, can be utilized in the biomedical field (Laurencin *et al* 1999; Yeong K C B *et al* 2001). In this context, several macromolecules, such as stearic acid, monosaccharides and related molecules have been explored already with a desired control on the morphology. Hence, in order to control the size and morphology of HAp, we have chosen cetyl trimethyl ammonium bromide

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(CTAB) as a cationic surfactant, which was widely used to achieve control of the morphology in many aqueous synthetic methods.

Liu *et al* (2002) reported the synthesis of HAp nanofibres with diameter of 5–8 nm and length of 160–220 nm using the templates such as CTAB, polyethylene glycol (PEG) and cyclohexane. In a similar manner, Sun *et al* (2006) reported the synthesis of single crystal HAp nanorods with diameter, 8–15 nm and length, 25–30 nm by using the quaternary reverse microemulsion (TX-100+CTAB/*n*-butanol+*n*-exanol/cyclohexane/water) method. Another method like hydrothermal microemulsion was proposed by Kalita *et al* (2007) for the synthesis of nanohydroxyapatite rods using CTAB as the surfactant and *n*-pentanol as the cosurfactant. However, the foresaid researchers neither used CTAB alone as a template nor optimized its concentration on the size and morphology of the as-synthesized HAp during synthesis.

Arami *et al* (2009) reported the synthesis of hydroxyapatite nanostrips by using microwave heating method and CTAB as a template. But the effect of CTAB concentration on phase purity, crystallinity and morphology of the as-synthesized HAp using this microwave heating method was not investigated. On the other hand, Yan *et al* (2001) reported the synthesis of HAp nanorods using surfactants, CTAB and sodium dodecylsulphate (SDS), under hydrothermal conditions at 150 °C. However, they failed to attempt the effect of surfactant concentration on morphology of the as-synthesized HAp. Salarian *et al* (2009) also reported the synthesis of hydroxyapatite nanorods by surfactant-assisted hydrothermal method. In their synthesis, CTAB acts as a soft template and PEG 400 acting as a co-template. They investigated mainly the effect of hydrothermal temperature alone on composition, size and morphology of as-synthesized HAp.

Motivated by the above, in this paper, we focus our attention to investigate the effect of various concentrations of CTAB as an only surfactant on the structural growth of nanohydroxyapatite using microwave irradiation method. Through our systematic investigation, it was found that fine adjustments in the surfactant concentrations under microwave irradiation method effectively modify the size as well as shape of nanohydroxyapatite particles. The influence of varying concentration of CTAB under microwave irradiation method on morphology and size of the nanohydroxyapatite particles is studied and presented.

2. Experimental

Analytical grade calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Merck, India) and dipotassium hydrogen phosphate ($\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, Merck, India) were used as precursors for calcium and phosphate, respectively. Along with this, Analar grade ammonia (Merck, India) and CTAB (Merck, India) were also used in the synthesis of HAp.

The precursor solutions were prepared by dissolving $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ (0.024 M) and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.04 M)

(Merck, India) in double distilled water. At first, 50 mL of 0.024 M $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ solution containing various concentrations (0.0012 M–0.24 M) of CTAB was prepared under constant stirring at 50 °C for 30 min to ensure cooperative interaction to accomplish self-assembling process. This was followed by the gradual addition of 50 mL of calcium nitrate solution (0.04 M) and the resultant mixture was mixed thoroughly with magnetic stirring. pH of the solution was then adjusted to 9 by adding NH_3 . The white suspension thus obtained was put in a teflon vessel, sealed tightly and heated by microwave irradiation (2.45 GHz, 900 W, LG, India) for 30 min. The white precipitate formed was gently washed with double distilled water to remove the residual CTAB and then dried at 80 °C for 12 h. The obtained powders were then calcined in a muffle furnace at 900 °C for 2 h. The above experiment was repeated for three times in order to get reproducibility of the results.

The as-synthesized nanohydroxyapatite particles were characterized by Fourier transform infrared spectroscopic (FT-IR) technique (Nicolet 380 FT-IR spectrophotometer) over the wavenumber ranging from 4000 to 400 cm^{-1} with 32 number of scans and a resolution of 4 cm^{-1} . For this, a small amount of HAp powder (~2 mg) was blended with KBr and then pressed into discs and FT-IR spectrum was recorded.

Phase composition and crystallinity of the calcined HAp particles were determined by X-ray diffraction (XRD, Bruker D-8 Advance, Germany) with $\text{CuK}\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$, generated at 35 kV and 25 mA. Data were collected over 2θ range of 20–60° with a step size of 0.010° and a count time of 0.2 s.

The fraction of crystallinity, X_c , of the nanohydroxyapatite powders was determined (Degirmenbasi *et al* 2006; Gopi *et al* 2010a, b, 2012) from the following equation:

$$X_c = (0.24/\beta)^3, \quad (1)$$

where β is the full width at half maximum (FWHM) for the diffraction peak under consideration.

Morphology and microstructure of the as-synthesized powders were characterized by scanning electron microscope (SEM, JEOL, Japan) and transmission electron microscopic (TEM) images were obtained from Philips CM12 transmission electron microscope operating at 120 kV.

3. Results and discussion

Figure 1(a–c) shows FT-IR spectra of the nanohydroxyapatite powders synthesized at various concentrations of CTAB and calcined at 900 °C for 2 h. It is observed that ν_1 vibration mode of the phosphate group is found around 960 cm^{-1} and ν_2 mode of the phosphate group appears at 472 cm^{-1} . The peaks around 1030 and 1080 cm^{-1} are due to ν_3 mode of the phosphate group while the peaks at 560–606 cm^{-1} correspond to ν_4 mode of the phosphate group. The broad band around 3420 cm^{-1} is due to the adsorbed lattice water and a peak at 1636–1641 cm^{-1} is due

Figure 1. FT-IR spectra of HAP nanoparticles synthesized in presence of different CTAB concentrations: (a) 0.0012 M, (b) 0.012 M, (c) 0.024 M and (d) 0.24 M.

Figure 2. XRD patterns of uncalcined HAP nanoparticles synthesized in presence of different CTAB concentrations: (a) 0.0012 M, (b) 0.012 M, (c) 0.024 M and (d) 0.24 M.

to O–H bending mode. Furthermore, OH stretching is found around 3561 cm^{-1} . It could also be observed that no peaks corresponding to CTAB could be detected in the spectrum indicating purity of the samples synthesized. For all the concentrations, the spectra showed well-resolved peaks indicating the formation of pure HAP particles. The spectra showed all the prominent peaks that are attributable to HAP powders as reported already in the literature (Rehman and Bonfield 1995) and the results observed were also consistent with our previous studies (Gopi *et al* 2008, 2009, 2010a, b, 2012).

Figure 2 shows XRD patterns of uncalcined HAP nanoparticles synthesized at various concentrations of CTAB. In all CTAB concentrations, the characteristic peaks appearing in the XRD pattern shown in figure 2(a–d) are attributed to HAP reflections and no characteristic peaks of impurities are

Table 1. Crystallinity of uncalcined HAP synthesized from various concentrations of CTAB.

Sample conditions	Plane	Line width (FWHM)	Fraction of crystallinity (X_c)
0.0012 M	(0 0 2)	0.222	1.26
0.012 M	(0 0 2)	0.219	1.32
0.024 M	(0 0 2)	0.215	1.39
0.24 M	(0 0 2)	0.208	1.53

Figure 3. XRD patterns of calcined HAP nanoparticles synthesized in presence of different CTAB concentrations: (a) 0.0012 M, (b) 0.012 M, (c) 0.024 M and (d) 0.24 M.

observed which are well consistent with ICDD card no. 09-0432. There are no differences except the intensity observed in XRD patterns between the samples synthesized at different concentrations of CTAB. From figure 2(a–d), it is evident that the intensity of diffraction peaks increase with an increase in CTAB concentration which strongly suggest the increased crystallinity of the as-synthesized HAP sample, i.e. there is also a sign of directional growth in XRD patterns. In a standard HAP pattern, the intensity of diffracted X-rays corresponding to (211) and (002) planes are assumed to be 100 and 40 units, respectively thus the ratio $I(211)/I(002)$ is equal to 2.5. In the case of HAP synthesized with 0.0012 M concentration of CTAB, intensity of the diffracted peaks corresponding to planes (002) and (211) are measured to be 20.4 and 64 units, respectively and the ratio $I(211)/I(002)$ is 3.1. Whereas, for the HAP synthesized with different CTAB concentrations such as 0.012, 0.024 and 0.24 M, the ratio of $I(211)/I(002)$ are found to be 3.20 (69/21.5), 3.25 (71.56/22.01) and 3.38 (75.52/22.3), respectively. Increase

in the crystallinity for the uncalcined HAP samples synthesized at various CTAB concentrations is further substantiated by the calculated crystallinity values from XRD results. The diffraction peak at (0 0 2) plane was chosen for the calculation of crystallinity since, it is sharper and isolated from others and the results are presented in table 1.

XRD patterns obtained for HAP powders using all studied concentrations of CTAB followed by calcination at 900 °C for 2 h are presented in figure 3. All the peaks detected are attributed to HAP. An increase in peak's intensity could also be observed upon increasing CTAB concentration owing to a concomitant increase in crystallinity. In particular, the diffraction peak at 25.875° corresponding to the plane (0 0 2) are sharp and their relative intensity are far greater than the standard value and are found to be 41.26, 42.18, 46.38 and 48.52, for 0.0012, 0.012, 0.024 and 0.24 M CTAB concentrations, respectively. Therefore, the corresponding ratio of $I(211)/I(002)$ is 1.58 (65.23/41.26), 1.62 (68.36/42.18), 1.94 (90.102/46.38) and 1.86 (90.38/48.52), respectively. This finding strongly reveals the increased crystallinity of the as-synthesized sample and the longitudinal direction of HAP

nanorods as well as nanofibres are in (0 0 2) plane, and they are oriented to grow along the *c*-axis more preferentially. Moreover, crystallinity of the HAP increases as the concentration of CTAB increases which is evidenced from the calculated crystallinity values presented in table 2. This is in conformation with TEM results that will be discussed later. Our XRD results are in excellent agreement with the standard diffraction data (ICDD file no. 09-0432).

The synthesis process at each concentration of CTAB was repeated for three times in order to check reproducibility of the results. But the morphological images of the obtained nanostructure at various concentrations of CTAB are presented only for one trial which is shown in figure 4. The shape, size, aspect ratio and standard deviation of the obtained nanostructures are discussed in detail as follows. When CTAB concentration was maintained at 0.0012 M, which is much closer to the critical micelle concentration (CMC) (Delsanti *et al* 1993), the particles were almost spherical in shape (figure 4(a)). This could be explained in view of the fact that, at CMC, CTAB in aqueous solution forms spherical micelles and, therefore, the obtained particles were essentially spherical and size of the particles ranges from 69–102 nm with a mean size of 83.4 nm and 9.066 is its standard deviation. On increasing the concentration of CTAB, shape of the micelle was transformed into an elongated one which is supported from the formation of slightly elongated nanorod structures as seen in figure 4(b). But its formation is not uniform throughout and size of the nanorods ranging from 535.67–768.08 nm in length and 80.16–95.07 nm in diameter with a standard deviation of 0.773 and the mean length, diameter and aspect ratios being 589.65, 88.54 and 6.7 nm, respectively.

Table 2. Crystallinity of calcined HAP synthesized from various concentrations of CTAB.

Sample conditions	Plane	Line width (FWHM)	Fraction of crystallinity (X_c)
0.0012 M	(0 0 2)	0.105	11.93
0.012 M	(0 0 2)	0.101	13.41
0.024 M	(0 0 2)	0.097	15.14
0.24 M	(0 0 2)	0.091	18.33

Figure 4. SEM images of HAP nanoparticles synthesized in presence of different CTAB concentrations: (a) 0.0012 M, (b) 0.012 M, (c) 0.024 M and (d) 0.24 M.

Whereas, uniform HAP nanorods (figure 4(c)) with length and width ranging from 884.14–1000 and 80.12–100 nm and a standard deviation of 0.456 could be achieved for a CTAB concentration of 0.024 M. The nanorods obtained are much thinner, longer with uniform size distribution and are random in orientation. From this micrograph, it is clearly evident that the mean average diameter, mean length and mean aspect ratio were found to be 91.46 nm, 936.43 nm and 10.2, respectively. On further increasing the concentration of CTAB to 0.24 M, shape of the HAP nanorods is transformed to nanofibres (figure 4(d)) owing to the change in fibre-like micellar structure of CTAB.

Figure 5. (a) TEM images for HAP nanofibres and (b) HRTEM image of a single nanofibre (inset: electron diffraction pattern).

TEM images of the HAP nanofibres obtained from 0.24 M concentration of CTAB is shown in figure 5. As seen from the image, it was estimated that length and diameter of the nanofibres ranged from 45.38–120.13 nm and 3–5 nm (figure 5(a)) with a standard deviation of 9.261. HAP nanofibres were straight and long with mean length and diameter of 90.78 and 3.93 nm, respectively, resulting in a very large aspect ratio of around 24.6 which were well consistent with the previously reported results (Liu *et al* 2002). The high resolution transmission electron microscopic (HRTEM) image shows uniform lattice array of atoms (figure 5(b)). Moreover, the resultant nanofibres showed good crystallinity which is evident from the obtained electron diffraction (figure 5(b) inset) pattern. The above morphological results and the mean, standard deviation of the reproduced results reveal that the size and morphology of the as-synthesized HAP particles can be effectively controlled by tuning the concentration of CTAB as an only surfactant used in this synthesis under microwave irradiation method. Liu *et al* (2005) emphasized that the presence of CTAB, PEG 400 and ethanoic acid are crucial for the formation of HAP nanorods. But in our system, there is no need to use the other co-surfactants like PEG, TX-100, ethanoic acid, ammonium nitrate and other oil phase systems such as cyclohexane, *n*-pentanol, *n*-butanol, *n*-hexanol to control the microstructure of as-synthesized HAP as reported by other workers previously (Liu *et al* 2002, 2005; Kalita *et al* 2007; Salarian *et al* 2009). Further, there is no need to use high reaction temperature ranging from 90 to 150 °C for the synthesis of pure HAP nanorods and nanofibres (Yan *et al* 2001; Wang *et al* 2006; Salarian *et al* 2009). Moreover, in our study, we used microwave irradiation as an assistant technology which yields phase pure HAP nanostructures rapidly as evident from XRD results (figures 2 and 3) as discussed before and this method consumes less time compared to other conventional methods. Besides, it is interesting to note that the aspect ratio and crystallinity of the as-synthesized HAP nanostructures increase while changing the morphology from rod-like to fibre-like structure (table 2).

The growth modification achieved through CTAB addition could be explained as follows: at the critical micelle concentration (CMC) (0.001 M), the surfactant CTAB tends to form spherical-shaped micelle and resulting in the ingrowth of spherical-shaped nano-HAP particles (Lin *et al* 2007). In aqueous solutions, CTAB ionizes thoroughly and forms cations with tetrahedral structures similar to phosphate anions. Subsequent attachment of CTAB cations with phosphate anions results in spherical-shaped HAP owing to the

Figure 6. Schematic sketch showing charge to structure complementarity of surfactant.

Figure 7. Mechanism of formation of HAp nanospheres, nanorods and nanofibres through different CTAB micelle structures.

appropriate charge and structure complementarity as shown in figure 6 (Shih *et al* 2004; Sun *et al* 2007).

When the concentration of the surfactant is maintained above its CMC, CTAB tends to form rod-like micelles (Wang *et al* 2006). The micelles act as nucleating points for the growth of HAp crystals and during the reaction, CTAB–HAp complexes are produced and they coalesce to control the morphology and size of obtained HAp. Since the crystallization process is under critical control of CTAB concentration, the resulting HAp consisted invariably of nanorods with uniform morphology and controllable size.

On further increasing the concentration of CTAB above its CMC, size of the micelles increased eventually resulting in long, flexible worm-like micelles (Han *et al* 2003) and hence, the ingrowth of HAp nanofibres are facilitated and these structures could be obtained at a much higher concentration (0.24 M). The growth of micelles leads to an elongated structure that can occur by two mechanisms (Salarian *et al* 2009). In the first, there may be an internal driving force which causes the formation of large aggregates with a different geometry. Whereas, in the other mechanism, the micellar growth was induced by the repulsions of the intermicelles when the micelles come in direct or close contact which allows a better packing of the micelle and this phenomenon occurred at high concentrations of CTAB. Hence, the surfactant (CTAB) plays the role of a template for the overall synthesis of nanohydroxyapatite spheres, rods and fibres (figure 7). Since bone is a composite of natural fibres like collagen, these fibrous-like nanobiomaterials could enhance

bone formation and tissue regeneration when employed in biomedical applications.

4. Conclusions

Nano-sized HAp particles with different growth modifications were successfully achieved through a rapid hydrothermal technique using CTAB as an only surfactant. The surfactant acted as a template for the overall synthesis of fine nano-sized spheres, rods and fibres and the assistance of microwave irradiation resulted in rapid formation of nanohydroxyapatite. FT–IR and XRD results prove the formation of pure hydroxyapatite particles and complement each other in confirming quality of the product. SEM results have depicted the formation of spherical, rod-like and fibre-shaped HAp particles. The growth of HAp nanofibres is evident from TEM evaluations. Such nanomaterials with designable structures could be potential candidates for coating implant materials intended for biomedical applications.

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