

Surfactant-assisted synthesis and characterization of hydroxyapatite nanorods under hydrothermal conditions

M. SALARIAN^{1*}, M. SOLATI-HASHJIN², S. SARA SHAFIEI²,
A. GOUDARZI², R. SALARIAN³, A. NEMATI⁴

¹School of Engineering, School of Materials Engineering, Tehran Science and Research Branch,
Islamic Azad University, Tehran, Iran

²Biomedical Engineering Faculty, Amirkabir University of Technology, Tehran, Iran

³Maziar University, School of Engineering, Mazandaran, Noor, Iran

⁴School of Materials Science and Engineering, Sharif University of Technology, Tehran, Iran

Hydroxyapatite (HAp) nanorods with uniform morphology and controllable size were successfully synthesized by precipitating $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ in the presence of cetyltrimethylammonium bromide (CTAB) and polyethylene glycol 400 (PEG 400) as cationic surfactant and non-ionic co-surfactant, respectively, under hydrothermal conditions. The effect of hydrothermal temperature on the composition, morphology and size of HAp particles was studied using X-ray diffraction (XRD), Fourier transform infrared spectrometry (FTIR) and scanning electron microscopy (SEM). Results revealed that the morphology and size of HAp particles can be effectively controlled by the presence of CTAB and PEG surfactants. In addition, the temperature of the hydrothermal treatment plays an important role in controlling the morphology and size of HAp particles. The aspect ratio of rod-like particles increases with the increase in the hydrothermal temperature. Moreover, the crystallinity of HAp powders increases with the increase in the hydrothermal temperature. The template action of CTAB and the co-template action of PEG 400 used to regulate the nucleation and crystal growth are also discussed.

Key words: *nanorods; hydroxyapatite; surfactant; morphology*

1. Introduction

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAp) nanoparticles have been of great interest because their mineral components are similar to human hard tissues [1–3]. Synthetic

*Corresponding author, e-mail: mehrnazsalarian@gmail.com

HAp has excellent biocompatibility and bioactivity, thus it is used in the reconstruction of damaged bone or teeth [4, 5]. The principal limitation in its clinical use as a load bearing implant is its mechanical brittleness. Generally, the fracture strength and fracture toughness of ceramic materials are effectively improved by dispersing rod-like crystals and thin filaments into the bulk materials. Thus, HAp rod-like crystals and whiskers do appear to be useful as materials for improving the mechanical properties of synthetic biomaterials, etc. [6–8].

It is well-known that the strength of ceramic fibres and whiskers is size-dependent. As the diameter or length decrease, the strength of ceramic fibres and whiskers increases. Moreover, their physical properties such as fracture toughness and fracture strength depend on the crystal structure, composition and sizes [9].

HAp can be synthesized by many chemical processing routes such as solid state reaction [3, 10], coprecipitation and hydrothermal technique [11, 12]. Solid state reactions usually give stoichiometric and well-crystallized products but they require relatively high temperatures and long heat-treatment times. Moreover, the sintering capacity of such powders is usually low and ultimately results in inferior mechanical properties of the sintered matrices [8, 12]. In the case of coprecipitation, nanometer size powders can be prepared. However, their crystallinity and Ca/P ratio depend mainly upon the preparation conditions and are in many cases lower than for well-crystallized stoichiometric HAp. The hydrothermal technique usually results in HAp powders with a high degree of crystallinity and the Ca/P ratio close to the stoichiometric value [8, 12]. However, the obtained powders have typical agglomeration and their size distribution is relatively wide. Therefore, the size distribution of HAp powders cannot be well controlled using the normal hydrothermal method [12]. A newly developed hydrothermal technique that is used to synthesize nanopowders, nanorods and nanoneedles [1, 8, 13] is the surfactant-assisted hydrothermal method. This method inhibits the excess agglomeration of the particles, since the surfactants can adsorb on the surface of particles. In addition, the surfactants can serve as a versatile “soft” template for the synthesis of 1 D nanostructured materials [8, 14]. Furthermore, the hydrothermal treatment can effectively increase the crystallinity of the product [8].

In this study, hydroxyapatite nanorods with uniform morphology and controllable size have been successfully synthesized in the presence of cetyltrimethylammonium bromide (CTAB) acting as a soft template and polyethylene glycol 400 (PEG 400) acting as a co-template. Also, the effect of hydrothermal temperature on the composition, morphology and size of hydroxyapatite particles is investigated.

2. Experimental

Materials and methods. The starting materials used in this study were calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) (Merck Prolabo 22 384.298), diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) (Merck Prolabo 21 306.293), cetyltrimethylammonium bromide (CTAB) (Merck 102342) and polyethylene glycol (PEG 400) (Merck

807485). All chemicals were of analytical grade. The Ca/P molar ratio was equal to 1.67 (stoichiometric ratio of HAp).

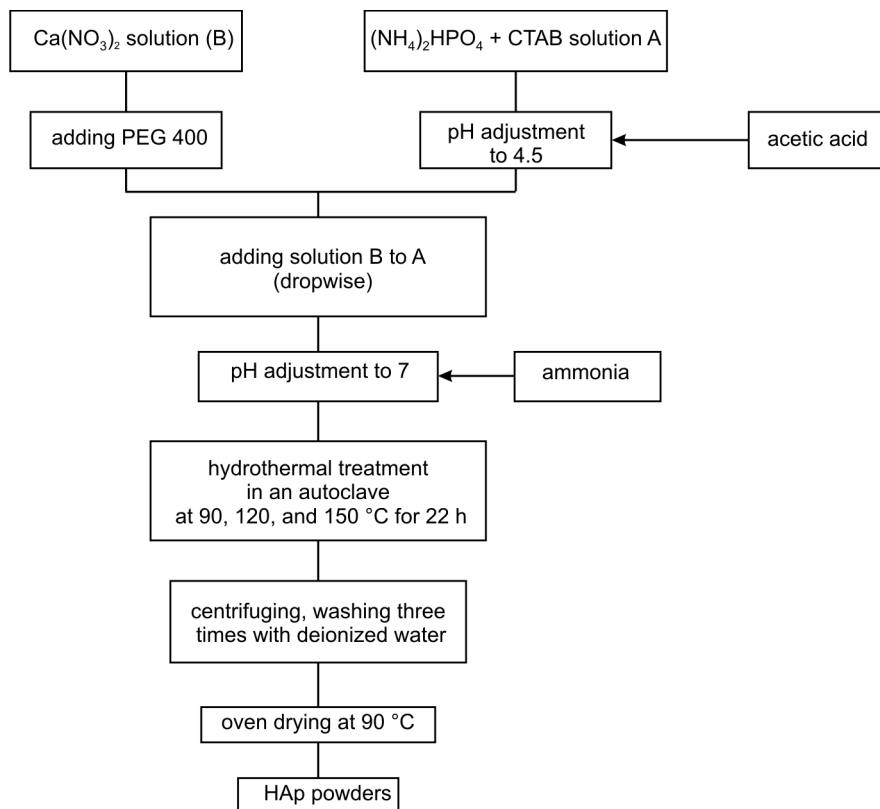


Fig. 1. The process flowchart for synthesis of HAp nanorods

The general procedure was the following: 0.03 mole of $(\text{NH}_4)_2\text{HPO}_4$ and 0.021 mole of CTAB were dissolved in 125 ml of deionized 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 the pH value was adjusted to 4.5 by adding pure acetic acid. After that, 0.05 mole of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 175 ml of deionized water and 50 ml of PEG 400 was simultaneously added to the solution under constant stirring for 30 min. Then the mixed solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and PEG 400 were added to the latter dropwise under continuous magnetic stirring in air. pH of the solution was adjusted to 7 using ammonia. The final milky suspension was transferred to a stainless steel autoclave, sealed tightly and hydrothermally treated in an oven at 90, 120 and 150 °C for 22 h. The resulting precipitates were separated from the suspension by centrifuging, washed three times with deionized water to remove the residual CTAB and PEG 400, and then oven dried at 90 °C for 22 h to yield white powders. The flowchart for HAp nanorod synthesis is shown in Fig. 1.

Characterization. The crystallographic structural analysis was carried out by X-ray diffraction (XRD) method using a D4 Bruker powder diffractometer with monochromatic CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$) over the 2θ range of $10\text{--}70^\circ$ at a scan rate of $1^\circ/\text{min}$ in the Guinier geometry. The operational voltage and the current were 40 kV and 30 mA, respectively. Fourier transform infrared (FT-IR) spectroscopy (Bruker IFS 48) was used to identify the functional groups. The potassium bromide (KBr) disk technique was used for the analysis, using 2 mg of HAp powders compacted under hydraulic pressure with 200 mg of KBr. The spectrum was recorded in the $4000\text{--}400 \text{ cm}^{-1}$ region with 2 cm^{-1} resolution averaging 100 scans.

The morphology and size of HAp particles were investigated by a XL30 Philips scanning electron microscopy (SEM). The powders for SEM analysis were prepared by sprinkling the dried HAp onto one side of a double adhesive tape, which was stuck to an aluminum stub. The stub was then gold coated using EMITECH K450X (England) to a thickness of 20–30 nm and examined with an accelerating voltage of 20 kV.

3. Results

Typical XRD patterns of the HAp samples obtained at 90, 120 and 150 °C are shown in Fig. 2. Phase identification of the synthesized powders was accomplished by comparing the experimental XRD patterns with the database compiled by the Joint Committee on Powder Diffraction Standards (JCPDS), namely the following card numbers: 9-432 for HAp, 9-169 for whitlockite ($\beta\text{-Ca}_3(\text{PO}_4)_2$) and 9-80 for monetite (CaHPO_4). In general, the XRD patterns exhibit characteristic peaks of HAp but some differences may be observed. The XRD pattern of the HAp powder obtained at 150 °C (Fig. 2, curve A) contains sharp peaks which can be perfectly matched to crystalline HAp with no additional peaks, while those obtained at 120 °C and 90 °C (curves B and C) contain some peaks corresponding to whitlockite and monetite structures. At 150 °C, no impurity other than HAp is detected by the XRD, which indicates that the product is monophase of HAp. Thus we may conclude that HAp powders do not crystallize completely below 150 °C.

There is also a sign of directional growth in the XRD patterns. In a standard HAp pattern, the intensity of diffracted X-rays corresponding to the (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 HAp powder synthesized at 150 °C, the diffraction peak corresponding to (002) is sharp, and its relative intensity is far greater than the standard value ($I_{211}/I_{002} = 1.85$). This indicates that the (002) surface is more fully grown in this sample; in other words, HAp nanorods are oriented to grow along the c axis. For the HAp samples obtained at 120 °C and 90 °C, the $I_{(211)}/I_{(002)}$ ratios are 2.1 and 2.2, respectively. The results indicate that in all samples, the longitudinal direction of rod-like HAp is [002], and the directional growth along the c axis is more prominent in HAp powders synthesized at 150 °C as will be seen in the SEM photographs.

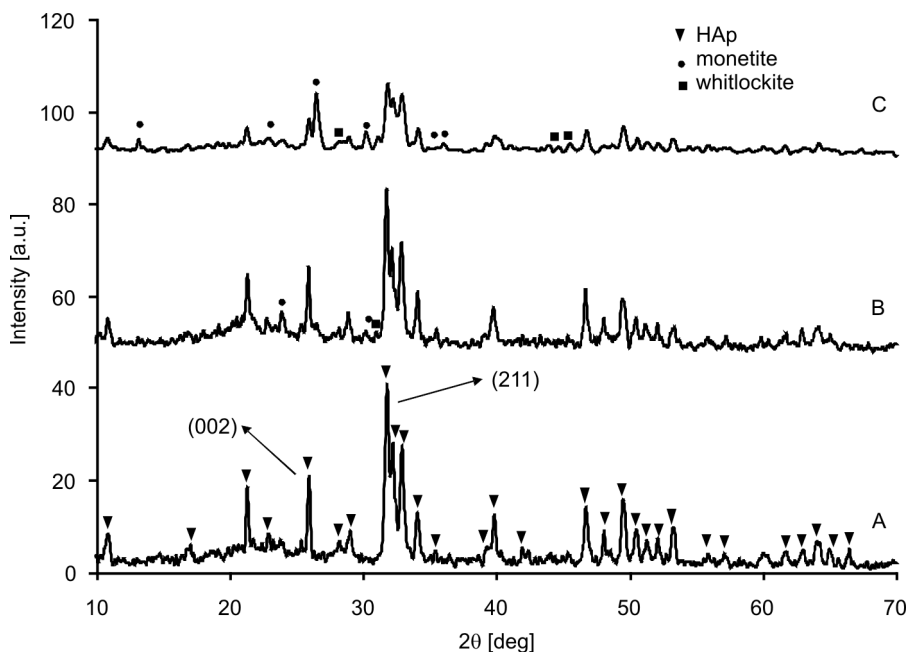


Fig. 2. Typical XRD patterns of HAp powders obtained at: 150 °C (A), 120 °C (B) and 90 °C (C)

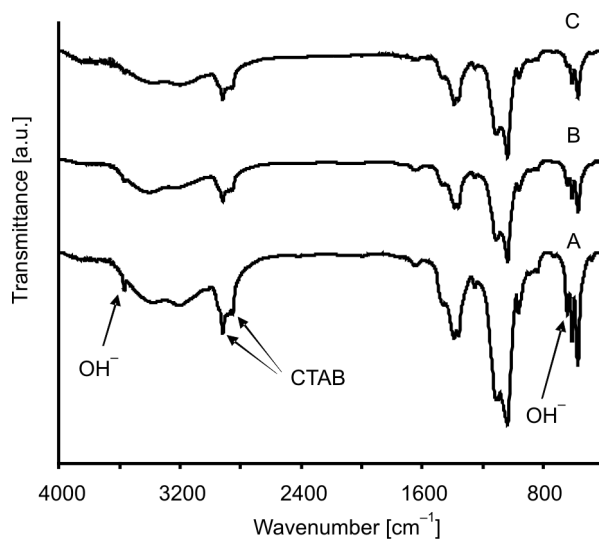


Fig. 3. Typical FTIR spectra of HAp powders obtained at: 150 °C (A), 120 °C (B) and 90 °C (C)

Figure 3 shows typical FTIR absorption spectra of the HAp samples synthesized at 90, 120 and 150 °C. In general, the FTIR spectra of all samples display the same profile. In all these HAp powders, absorption peaks at 1460, 882 and 670 cm^{-1} are as-

signed to carbonate ions [15, 16] which reveal that a certain level of carbonate substitution takes place in these samples, although this is not shown by the XRD phase analysis. The carbonate ions may come from a reaction between atmospheric carbon dioxide and solution during the synthesis process. The C–H stretching vibration bands appearing at 2851 and 2916 cm^{-1} are attributed to residual CTAB [9, 17] which show that the organic surfactant has not been completely washed away and remains in the obtained samples.

By a simple heat treatment (1 h at 450 °C), the residual organic materials will be removed. The characteristic bands for PO_4^{3-} appeared at 471.2 ($\nu_2 \text{PO}_4^{3-}$ [18]), 565 and 602.7 ($\nu_4 \text{PO}_4^{3-}$ [19]), 962 ($\nu_1 \text{PO}_4^{3-}$ [5, 19]), 1031 and 1095 ($\nu_3 \text{PO}_4^{3-}$ [20]), and 1248 cm^{-1} (P–O stretching vibration of PO_4^{3-} [21]). The band at 1382 cm^{-1} is assigned to the N–O stretching mode of NO_3^- [22]. A broad band at 1633 and 3197 cm^{-1} corresponds to adsorbed water [9, 23], while the broad band at 3401 cm^{-1} may come from the H_2O lattice because this band exists in the range of 3550–3200 cm^{-1} for hydrated H_2O [9]. The medium band at 1355 is attributed to OH in-plane bend [9]. Two medium sharp peaks at 633 and 3570 cm^{-1} attributed to vibrational [24] and structural OH^- [20, 23] modes are better visible and sharper in the HAp sample obtained at 150 °C (Fig. 3, curve A) compared with the product obtained at 120 °C (Fig. 3, curve B), whereas for powders synthesized at 90 °C they are relatively indistinct (Fig. 3, curve C) which indicates a lower crystallinity of the product obtained at lower hydrothermal temperatures. Overall, it could be deduced that the crystallinity of the obtained powders increases with the increase in the hydrothermal temperature.

To screen the influence of surfactants on the morphology and size of HAp particles, the synthesis process was conducted with and without CTAB and PEG 400. Figure 4 shows the SEM micrographs of the sample synthesized at 150 °C in the absence of CTAB and PEG 400 and those obtained at 90, 120 and 150 °C in the presence of CTAB and PEG 400. As shown in the Fig. 4a, in the absence of both CTAB and PEG 400, the HAp particles are spherical with the diameter of about 50–80 nm. On the other hand, from the SEM photographs of HAp powders synthesized at 150 °C in the presence of both surfactants (Fig. 4b), the HAp particles have uniform, long, rod-like morphology with the typical diameter of about 50–80 nm and the average aspect ratio of about 16–20. For the HAp sample obtained at 120 °C (Fig. 4c), the rod-like particles with the mean particle size of about 80–120 nm in diameter and the aspect ratio of about 8–10 are clearly observed, but they are aggregated. At 90 °C, the product shows a plate-like structure and rod-like particles with the aspect ratio of about 6 and crystal diameter of about 100–120 nm, randomly distributed in the sample shown in Fig. 4d. HAp particles obtained at 150 °C are much thinner and longer; besides, nanorods have a more uniform size distribution, and are much more separated from each other compared with HAp samples obtained at 120 °C and 90 °C. Thus, we can conclude that the hydrothermal temperature plays a key role in the control of the crystal morphology and the crystal size.

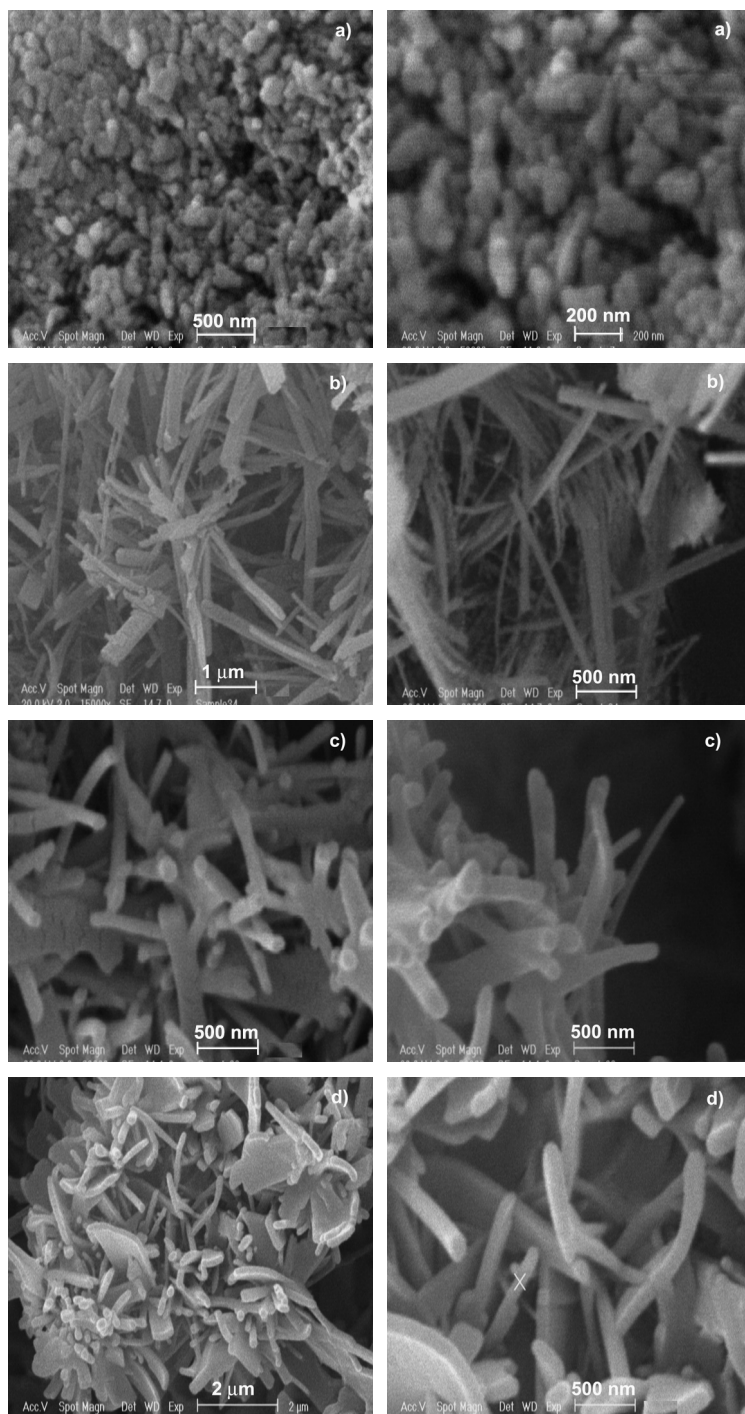


Fig. 4. Typical SEM photographs of the HAp powders obtained at 150 °C in the absence of CTAB and PEG 400 (a), in the presence of CTAB and PEG 400 at 150 °C (b), 120 °C (c), 90 °C (d)

4. Discussion

High temperature and high pressure of hydrothermal treatment could have two effects on the final products. Firstly, they might cause some fibres to aggregate, but the interaction between the aggregates would be so weak that they would tend to dissolve in the aqueous system. Secondly, they might raise the solubility of HAp to some extent and accelerate the dissolution and crystallization process. Also, the hydrothermal treatment can effectively increase the crystallinity of the product [8, 25].

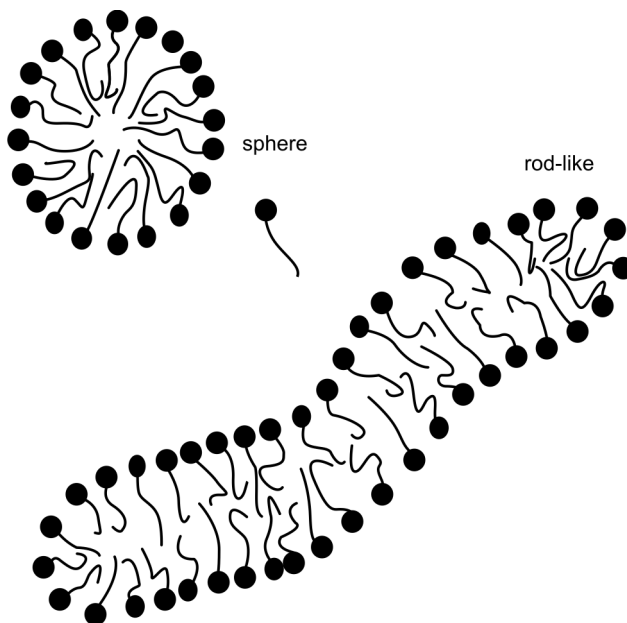


Fig. 5. The transition from a spherical micelle to a long rod- or thread-like micelle at high enough concentrations

The effect of CTAB on the HAp crystallization system is thought to act as a soft template [5, 8, 9], resulting in epitaxial growth of the product [5]. CTAB is a cationic surfactant and its critical micelle concentration (CMC) is 0.03% (0.9–1.0 mM) [9, 26]. Above the CMC, a transition from spherical micelles to rod-like micelles occurs and the size of micelles increases as the CTAB concentration increases, eventually resulting in long, flexible, thread-like micelles [27], as shown in Fig. 5. Micellar growth can be considered to arise from two mechanisms. In one mechanism, there is an internal driving force causing the formation of large aggregates with a different geometry. In the other mechanism, micellar growth is induced by intermicelle repulsions allowing a better packing of the micelles. This will occur at high concentrations, when the micelles come in direct, close contact. In our system, with the CTAB concentration of 0.168 M, micellar growth could easily result in long rod-like micelles. In an aqueous system, the CTAB would ionize completely and result in a cation with a tetrahedral

structure. Meanwhile, the phosphate anion has also a tetrahedral structure [5, 9]. Because of the complementary relationship between the charge and the stereochemistry, a process called molecule recognition could be realized at the inorganic/organic interface [28]. Thus, in that case, CTAB could be well incorporated in the phosphate anion [5]. When Ca^{2+} solution is added to PO_4^{3-} solution, $\text{Ca}_9(\text{PO}_4)_6$ clusters tend to form on the rod-shaped micellar surface, due to the conformation compatibility between the identical, hexagonal shapes of the micelles and the $\text{Ca}_9(\text{PO}_4)_6$ clusters. During the hydrothermal stage, CTAB–HAp complexes are formed and they coalesce to form nanorod structures. The micelles act as nucleating sites for the growth of HAp crystals [29, 30].

Particle formation is a very complex process, involving nucleation, growth, coagulation and flocculation. Addition of PEG can affect the nucleation during the crystallization process. After nucleation, PEG can influence particle growth, coagulation and flocculation [25]. Among common water soluble polymers, PEG is one of the most flexible polymers in an aqueous medium because of the flexible ether linkages in its backbone and the absence of bulky side groups. Thus, it is sterically less hindered in the aqueous medium [31, 32]. PEG can modify or control the surfaces of the nanometer crystals. In addition, PEG is a non-ionic surfactant able to form long chain structures in aqueous solution [9], and therefore it acts as a co-template. It has been reported that the PEG molecule has the ability to chelate Ca^{2+} [33, 34]; therefore, PEG–OH can attract Ca^{2+} released from $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ to form the bond of PEG–O– Ca^{2+} –O–PEG, then PEG–O– Ca^{2+} –O–PEG reacts with the PO_4^{3-} released from $(\text{NH}_4)_2\text{HPO}_4$ to produce HAp crystal nuclei [33]. Moreover, the most important role of the surfactant is to inhibit the excess aggregation of CTAB micelles, because the surfactant could adsorb on the surface of particles. As a result of their adsorption, an electrical double layer develops on the surfaces of solids or liquids. Adsorbed surfactant layers may involve micellar type structures and induce the formation of long, rod-like micelles. Therefore, we can reasonably assume that the template and co-template action endow the surfactants with the capability to control the crystallization and growth processes.

5. Conclusions

The morphology and size of hydroxyapatite crystals can be controlled by the presence of CTAB surfactant and PEG 400 cosurfactant under hydrothermal conditions.

The temperature of hydrothermal treatment plays a key role in the control of the morphology and size of the HAp crystal.

The high crystallization and homogeneity in the size distribution and the shape of the product obtained at 150 °C are attributed to the hydrothermal treatment and the soft template of the surfactants. The longitudinal direction of nanorods is [002], as confirmed by the XRD pattern of the samples.

The FTIR analysis proved that the products are carbonated apatite, although it was not shown by the XRD analysis. Since CHAp is known to be a better biomaterial than pure HAp, due to the similarity to the composition of biological apatite [23], the HAp powders obtained in this study are expected to show excellent bioactivity.

Using HAp nanorods as raw materials is an effective way to obtain dense bio ceramics with good mechanical properties. Therefore, the obtained HAp nanorods may be used as strength-enhancing additives for the preparation of HAp ceramics or bio-compatible nanocomposites with improved mechanical properties.

Acknowledgements

The authors express their gratitude to Prof. F. Moztarzadeh for supplying the necessary equipment.

References

- [1] SUN Y., GUO G., WANG Z., GUO H., *Ceram. Int.*, 32 (2006), 951.
- [2] HENCH L.L., *J. Am. Ceram. Soc.*, 74 (1991), 1487.
- [3] ELLIOTT J.C., *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates*, Elsevier, Amsterdam, 1994.
- [4] GROOT K.D., *Bioceramics of Calcium Phosphate*, CRC PRESS, Boca Raton, 1983.
- [5] WANG Y., ZHANG S., WEI K., ZHAO N., CHEN J., WANG X., *Mater. Lett.*, 60 (2006), 1484.
- [6] MIZUTANI Y., UCHIDA S., FUJISHIRO Y., SATO T., *Brit. Ceram. T.*, 97 (1998), 105.
- [7] YASZEMSKI M.J., PAYNE R.G., HAYES W.C., LANDER R., MIKOS A.G., *Biomaterials*, 17 (1996), 175.
- [8] LIN K., CHANG J., CHENG R., RUAN M., *Mater. Lett.*, 61 (2007), 1683.
- [9] LIU Y., HOU D., WANG G., *Mater. Chem. Phys.*, 86 (2004), 69.
- [10] MURUGAN R., RAMAKRISHNA S., *Comp. Sci. Technol.*, 65 (2005) 2385.
- [11] NARASARAJU T.S.B., PHEBE D.E., *J. Mater. Sci.*, 31 (1996), 1.
- [12] BYRAPPA K., *Handbook of Hydrothermal Technology*, William Andrew Publishing, LLC/Noyes Publications, New Jersey, 2001.
- [13] YAN L., LI Y., DENG Z., ZHUANG J., SUN X., *Int. J. Inorganic Mater.*, 3 (2001), 633.
- [14] MELDRUM F.C., KOTOV N.A., FENDLER J.H., *J. Phys. Chem.*, 98 (1994), 4506.
- [15] LIU J.B., YE X.Y., WANG H., ZHU M.K., WANG B., YAN H., *Ceram. Int.*, 29, (2003), 629.
- [16] ZAPANTA L.R., *Nature*, 403 (1965), 206.
- [17] KANDORI K., HORIGAMI N., YASUKAWA A., ISHIKAWA T., *J. Am. Ceram. Soc.*, 80 (1997), 1157.
- [18] FOWLER B.O., *Structural Properties of Hydroxyapatites and Related Compounds*, MD, Gaithersburg, 1968.
- [19] HE Q.J., HUANG Z.L., *Cryst. Res. Technol.*, 42 (2007), 460.
- [20] PANDA R.N., HSIEH M.F., CHUNG R.J., CHIN T.S., *J. Phys. Chem. Solids*, 64 (2003), 193.
- [21] BLAKESLEE K.C., CONDRAE R.A., *J. Am. Ceram. Soc.*, 54 (1971), 559.
- [22] ANEE T.K., ASHOK M., PALANICHAMY M., NARAYANA KALKURA S., *Mater. Chem. Phys.*, 80 (2003), 725.
- [23] CHENG Z.H., YASUKAWA A., KANDORI K., ISHIKAWA T., *J. Chem. Soc. Faraday Trans.*, 94 (1998), 1501.
- [24] LIAO C., LIN F., CHEN K., SUN J., *Biomaterials*, 20 (1999), 1807.
- [25] ZHANG F., ZHOU Z., YANG S., MAO L., CHEN H., YU X., *Mater. Lett.*, 59 (2005), 1422.
- [26] DELSANNTI M., MOUSSAID A., MUNCH J.P., *J. Colloid Interf. Sci.*, 157 (1993), 285.
- [27] HAN S.H., HOU W.G., DANG W.X., XU J., HU J.F., LI D.Q., *Mater. Lett.*, 57 (2003), 4520.
- [28] SHIH W., WANG M., HON M., *J. Cryst. Growth*, 275 (2005), 2339.

- [29] XIONG Y.J., XIE Y., YANG J., ZHONG R., WU C.Z., DU G.A., J. Mater. Chem., 12 (2002), 3712.
- [30] YAO J., TJANDRA W., CHEN Y.Z., TAM K.C., MA J., SOH V., J. Mater. Chem., 13 (2003) 3053.
- [31] WANG P., TAN K.L., KANG E.T., J. Biomat. Sci. Polym. E., 11 (2000), 169.
- [32] KIM B.S., HRKACH J.S., LANGER R., Biomaterials, 21 (2000), 259.
- [33] QIU C., XIAO X., LIU R., Ceram. Int., 30 (2007), 980.
- [34] HOSSAING S.F.A., HUBBELL J.A., Biomaterials, 15 (1994), 921.

Received 14 May 2008

Revised 12 November 2008