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Surfactant assisted synthesis of Hydroxyapatite using ultrasound method

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Abstract

Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ is one of the well-known bioceramic material which has its therapeutic applications as a bone substitute material because it is structurally similar to human bone. It also has excellent biocompatibility, bioactivity and surface-active properties with living tissues, osteoconductivity and non-toxicity. Particularly, this material is employed in orthopaedic and dental applications. In this research, hydroxyapatite powder was synthesized by adding Triton- X 100 as a surfactant through ultrasound method. By passing an ultrasound, HAP powder is obtained with high degree of crystallinity, purity with minimal agglomeration. The Ca/P ratio is very nearest to the stoichiometric value. This work reports synthesizing nano-HAP powder using surfactants through sonochemical method by tuning the experimental parameters such as irradiation time, temperature and concentration of the mixture. Owing to its bioactivity, it has been proven that surfactant assisted calcium phosphate synthesis structure gave pure nano-bioceramic powders with high degree of crystallinity after calcination. The as synthesised powder is to be tested further for this biocompatibility.

Keywords: Hydroxyapatite, Ultrasound, Triton X 100, Spherical, Plate.

1 Introduction

Hydroxyapatite is the main inorganic constituents of bone and teeth [1]. Hydroxyapatite is commonly referred to as HAP. Synthetic hydroxyapatite (HAP), ($Ca_{10}(PO_4)_6(OH)_2$) is commonly used in orthopaedic applications due to its very high biocompatibility, bioactivity, and osteoconductive properties and it favours the formation of new bone growth in osteoblastic cells [2-3]. Specifically, in orthopaedic applications, hydroxyapatite is used in a fabricated and sterilized form to improve the bioactive properties the importance of HAP has led to extensive research in numerous areas ranging from the physicochemical mechanisms of the formation to its applicability as a biomedical or industrial material [4-7]. In particular, the biocompatibility and osteoconductive properties of HAP have made it useful as implant material. New developments on the production of nano-sized HAP particles have led to many new applications. For example, nano-sized HAP particles can retard the multiplication of cancer cells and be used as an efficient drug delivery agent [8-9]. In orthopaedic applications, hydroxyapatite is used in a fabricated and sterilized form to improve the bioactive properties. The structural and morphological properties depends on temperature, time and ratio of calcium phosphate solutions. There are a number of significant advantages by using synthetic HAP in hard tissue industrial applications due to its good biocompatibility and bioactive properties with respect to bone cells and other body tissues, a slow biodegradability in situ and it also offers good osteoconductivity and osteoinductivity capabilities [10 - 12]. The various techniques used for the preparation of nano-hydroxyapatite includes, combustion synthesis[13], hydrothermal synthesis [14], mechanochemical synthesis [15-16], sol-gel [17], precipitation [18,19], and various wet chemistry techniques [20-21]. Now it has been reported that the surfactant assisted synthesis of hydroxyapatite using sonochemical method is the most promising method for the preparation of hydroxyapatite by novel morphologies and properties. It depends on the reaction stimulated by powerful ultrasound radiation leads to the creation of acoustic cavitation, continuous formation, growth and implosive collapse of the bubbles in a liquid [22-24]. It also stimulates the reaction between calcium and phosphate precursors accelerate the reaction rate in a significant manner [25-26]. Triton X 100 is a soluble and biodegradable nonionic surfactant. Triton X 100 increases the surface area of the hydroxyapatite by decreasing the size of the chief particles and by avoiding the agglomeration [27].

2 Experimental

Materials

Calcium nitrate tetrahydrate, Triton X 100 were purchased from Merck and Diammonium hydrogen phosphate were purchased from Sigma Aldrich.

Methods

Synthesis of HAP

The procedure for synthesis of HAP using ultrasound

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method as given below, Firstly, $Ca(NO_3)_2.4H_2O$ is dissolved in 20ml of double distilled water in a beaker and $(NH_4)_2HPO_4$ salt is dissolved in another beaker in 20 ml of double distilled water. Then 20ml of $(NH_4)_2HPO_4$ solution is added dropwise into the $Ca(NO_3)_2.4H_2O$ solution. The reactant mixture is stirred well for an hour. During stirring pH of 10 was maintained using NH_3 solution. The mixture was stirred for 2 hours and ultrasonicated for 40 minutes at 70°C. The sonicated reactant suspension was aged for one day. The obtained suspensions was filtered and washed several times with distilled water and ethanol to remove the impurities. The resultant powders are dried at 80°C for 6 hours in an oven. Then, finally the HAP powder was calcined for 3 hours at 750°C in muffle furnace. In a similar way, an experiment was conducted using Triton X 100(0.1g and 0.3 g) as a surfactant respectively.

3 Results and Discussion

3.1 FTIR studies

FT-IR spectrum of the HAP synthesized by ultrasound method in shown **fig 1(a-c)**. The spectrum shows all the characteristic peaks pertaining to the formation of HAP powders. The peak found at 3575 cm^{-1} indicates the stretching vibration of hydroxyl group [28]. In addition, the broad band centered approximately at 3400 cm^{-1} show the presence of adsorbed water. The strong absorption band appears at the range from 1055 cm^{-1} are attributed to asymmetric stretching mode of phosphate groups respectively. The peak at 600-574cm^{-1} are assigned to be an asymmetric bending mode of phosphate groups [29-30]. The absorption bands exhibits at around 959 cm^{-1} corresponds to symmetric stretching mode of phosphate groups. The peak at 470 cm-1 is attributed to υ_2 mode of phosphate group.

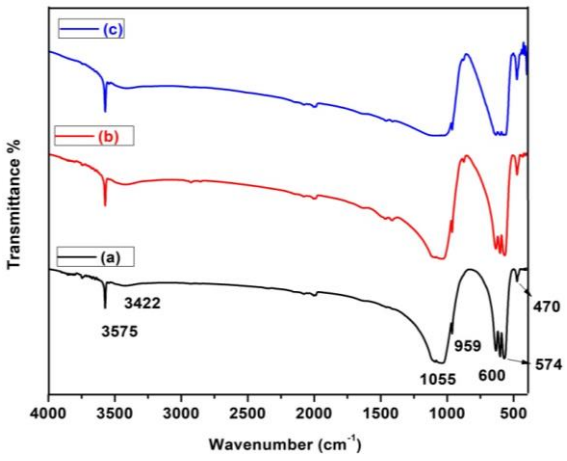

Figure 1. FTIR spectrum of (a) HAP (b) 0.1g Triton X 100 (c) 0.3g Triton X 100

All characteristic peaks of hydroxyl group and phosphate group for hydroxyapatite are present in FTIR spectrum. Hence it could be ascertained that the HAP sample obtained is pure. For the samples obtained with the addition of the surfactant (Fig. 1 (b & c), it could be observed that all the peaks corresponding to HAP was observed and no impurity peaks were detected in the spectrum which indicates that all the samples obtained were pure.

3.2 XRD studies

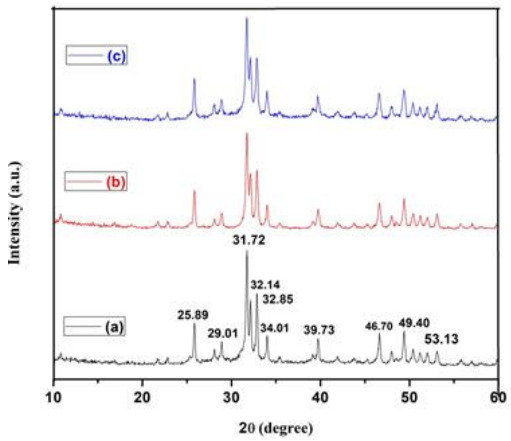

Figure 2. XRD spectrum of (a) HAP, (b) 0.1g Triton X 100 (c) 0.3g Triton X 100

Figure.2(a-c) indicates the XRD patterns for the HAP and surfactant assisted HAP in an ultrasound method. It is found that the XRD patterns of the HAP sample are in good agreement with standard value of JCPDS data base (09-0432) for HAP which indicated that the crystal structure of HAP sample is similar to the pure hydroxyapatite. The purity of powder is ascertained by adopting adequate sintering procedure for the sample whereby the phase purity of HAP powder is achieved. The grain size decreases by adding triton X 100 as an additive due to the reason that, increase in concentration of the surfactant, decrease in particle size decreases which is evident from table 1.

Table 1 Grain size for HAP and Triton X 100 assisted HAP, calculated using Scherrer equation

Sample code	2θ(degrees)	FWHM	Grain size(nm)
(a)	31.74	0.23	36
(b)	31.73	0.30	28
(c)	31.72	0.32	26

3.3 Scanning Electron Microscopic studies

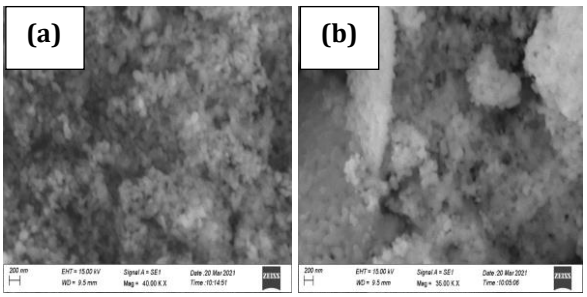

Figure 3. SEM micrographs of, (a) HAP, (b) Triton X 100 assisted HAP

In Fig (a), SEM image of hydroxyapatite composite shows an uniform spherical like morphology in the range

of 200nm. In fig (b) It has been observed that, the spherical shaped HAP converted into plate like morphology consist of fine clusters and the average particle size is around 200 nm. This suggests that the presence of Triton X 100 have the great influence on the morphology of the product due to interaction between surfactant and the calcium ions in the solution and on the surface of calcium phosphate particles.

4 Conclusions

The surfactant reinforced hydroxyapatite composite was successfully prepared by using ultrasound agitation method. In this work calcium nitrate tetra hydrate, diammonium dihydrogen phosphate is used as precursor materials and Triton X 100 as a surfactant. The incorporation of sonication process for preparing surfactant assisted hydroxyapatite composite with different concentrations are believed to change the morphological characteristics of hydroxyapatite composite with high purity and crystallinity were prepared by this method. It is also evident that, the particle size decreases by adding Triton X 100 to the HAP synthesis. Calcination was performed for this samples inorder to achieve good densification of samples The obtained product shows surfactant assisted hydroxyapatite with high purity and uniform size distributions.

Conflicts of Interest

The content, experimental data and the findings in this paper are original. It had no conflict of interest.

References

[1] S.V. Dorozhkin, M. Epple, Angew. Chem., Int. Ed. Engl. 41 (2002)3130–3146.

[2] H. Oonishi, Orthopaedic applications of hydroxyapatite, Biomaterial12 (1991) 171–178.

[3] L.L. Hench, Bioceramics—from concept to clinic, Journal of the American CeramicSociety74(1991)1487–1510.

[4] S. Koutsopoulos, E. Dalas, Langmuir 16 (2000) 6739.

[5] S. Koutsopoulos, E. Dalas, J. Colloid Interface Sci. 231 (2000) 207.

[6] S. Koutsopoulos, E. Dalas, Langmuir 17 (2001) 1074.

[7] H. Tanaka, K. Miyajima, M. Nakagaki, S. Shimabayashi, Chem. Pharm.Bull. 37 (1989) 2897.

[8] Y.F. Wang, Y.H. Yan, W. Ren, Trans. Nonferr. Met. Soc. China 14 (2004) 29–32.

[9] T.Y. Lu, S.Y. Chen, D.W. Liu, S.C. Liou, J. Control. Release 101 (2005)112–121.

[10] Blom A. Curr Orthopaed.21(4):280–287, 2007.

[11] Habibovic P, de Groot K. Osteoinductive biomaterials-properties and relevance in bone repair.J Tissue Eng and Regen Med; 1(1):25–32.2007

[12] Kalita SJ, Bhardwaj A, Bhatt HA. Materials Science and Engineering. 27(3):441–449. 2007.

[13] G. Gergely, F. Wéber, I. Lukács, A.L. Tóth, Z.E. Horváth, J. Mihály, C. Balázsi, Ceram. Int. 36 (2010) 803-806.

[14] S.-C. Wu, H.-K. Tsou, H.-C. Hsu, S.-K. Hsu, S.-P. Liou, W.-F. Ho, Ceram. Int.39 (2013) 8183-8188.

[15] W. Kim, Q. Zhang, F. Saito, J. Mater. Sci. 35 (2000) 5401-5405.

[16] K.C.B. Yeong, J. Wang, S.C. Ng, Biomaterials. 22 (2001) 2705-2712.

[17] G.S. K. Agrawal, D. Puri and S. Prakash, Journal of Minerals and Materials Characterization and Engineering, 10 (2011) 727-734.

[18] I. Mobasherpour, M.S. Heshajin, A. Kazemzadeh, M. Zakeri, J. Alloy. Compd. 430 (2007) 330-333.

[19] S.S.A. Abidi, Q. Murtaza, J. Mater. Sci. Technol. 30 (2014) 307-310.

[20] Y.X. Pang, X. Bao, J. Eur. Ceram. Soc. 23 (2003) 1697-1704.

[21] A.J. Nathanael, S.I. Hong, D. Mangalaraj, P.C. Chen, Chem. Eng. J. 173 (2011) 846 854.

[22] K.S. Suslick, Science 247 1439. 1990 82

[23] K.S. Suslick, S.B. Choe, A.A. Cichowlas, M.W. Grinstaff. Nature 353 (1991) 414.

[24] Y.Han,X. Wang,S. Li. Adv.Appl.Ceram.108(2009) 400-405.

[25] P. Rouhani, N. Taghavinia, S.Rouhani. Ultrason. Sonochem.17(2010)853-856.

[26] W. Kim, F.Saito. Ultrason.Sonochem. 8 (2001) 85-88.

[27] E. Iyyappan, P. Wilson, Ceram. Int. 39 (2013) 771–777.

[28] G.S. Kumar, G. Karunakaran, E.K. Girija, E. Kolesnikov, N. Van Minh, M.V. Gorshenkov, D. Kuznetsov, Ceram. Int. **44**, 11257–11264 (2018).

[29] B. Moreno-Perez, Z. Matamoros-Veloza, J.C. Rendon-Angeles, K. Yanagisawa, A. Onda, J.E. Perez-Terrazas, E.E. Mejia-Martinez, O.B. Diaz, M. Rodriguez-Reyes, Ceram. Vidr. **59**, 50–64 (2020).

[30] M.F. Alif, W. Aprillia, S. Arief, Mater. Lett. **230**, 40–43 (2018).