



P-ISSN: 2349-8528

E-ISSN: 2321-4902

www.chemijournal.com

IJCS 2021; 9(1): 2296-2298

© 2021 IJCS

Received: 04-11-2020

Accepted: 13-12-2020

Shiv Prakash MishraDepartment of Physics and
Electronics, Dr. Ram Manohar
Lohiya Avadh University,
Ayodhya, Uttar Pradesh, India**KK Verma**Department of Physics and
Electronics, Dr. Ram Manohar
Lohiya Avadh University,
Ayodhya, Uttar Pradesh, India

SEM image of transformed succinate ion mediated OCP to hexagonal HAP Nanocrystals

Shiv Prakash Mishra and KK Verma

DOI: <https://doi.org/10.22271/chemi.2021.v9.i1af.11569>

Abstract

In formation of laminated thin plate-shaped hydroxyapatite (HAP) nanocrystals from succinate ion based plate-shaped octacalcium phosphate (OCP) under hydrothermal condition which are performed at 180 °C for 3hour. The morphological observation of nanocrystals have been characterized by scanning electron microscope (SEM) and other using patterns as XRD, FTIR technique. The magnifying SEM images of synthesized samples are indicates the dark line observed at the centre of Suc-20 crystals during hydrothermally, which can attributed to the gap between two thin plate crystals, likely, hexagonal HAP nanocrystals generated from organically incorporated OCP by phase transformation.

Keywords: Hydroxyapatite, octacalcium phosphate, succinate ion

1. Introduction

The apatite are indispensable for which the general formula is $\text{Ca}_5(\text{PO}_4)_3\text{X}$, where $\text{X}=\text{F}$, Cl or OH , since they are key component of bone and teeth [1]. Recently, synthetic apatites that permit bone grafts are now available [2]. The hydroxyapatite ($\text{HAP}, \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) which is the main inorganic components of hard tissue such as bone and teeth and they are used in medicinal application have attracted a great attention including several application such as artificial organs, tissue engineering, medical devices & dentistry etc. [3,4]. Although, fabricated biological hydrogels loaded biphasic calcium phosphate nanoparticles have also been reported for bone tissue regeneration [5]. Especially, characteristics transformation behaviours of octacalcium phosphate (OCP, $\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$) to HAP have been reported, which has differences from other calcium phosphate compounds under hydrothermal conditions, (in *vitro* & *vivo*) [6-8]. The HAP may be prepared by various calcium orthophosphates such as α - & β -tricalcium phosphate (TCP, $\text{Ca}_3(\text{PO}_4)_2$) and OCP as well. For (α - β -) TCP, because HAP is transformed by solvation precipitation reaction, there is no correlation between the original TCP crystal particle's shape and the transformed HAP particle shape. Generally, forming of the spike or needle shaped HAP crystals from granular α - & β -TCP particles under hydrothermal conditions [9,10].

Herein, a plate-shaped OCP crystals are transformed to laminated thin plate- shaped HAP nanocrystals under hydrothermally and characterized the resultant HAP. The OCP crystal is composed of apatite and hydrated layers producing plate-shaped crystals [11, 12]. Where, the hydrogen phosphate ion (HPO_4^{2-}) in the hydrated layers can be substituted or incorporated by dicarboxylate such as succinate ions into OCP crystal structure has been reported [13, 14]. The molecular structure of succinic acid and there ion is shown in figure -1.

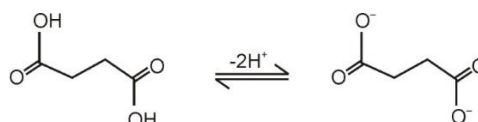


Fig 1: Structure of succinic acid ($\text{HOOC} \cdot (\text{CH}_2)_2 \cdot \text{COOH}$) & its succinate ion ($\text{OOC} \cdot (\text{CH}_2)_2 \cdot \text{COO}^{2-}$)

Corresponding Author:**Shiv Prakash Mishra**Department of Physics and
Electronics, Dr. Ram Manohar
Lohiya Avadh University,
Ayodhya, Uttar Pradesh, India

2. Experimental

The experimental procedure for organo-modified octacalcium phosphate (OCP, $(\text{HPO}_4)_2 \cdot (\text{PO}_4)_4 \cdot 5\text{H}_2\text{O}$) with incorporated succinate ion has been synthesized by a previously reported method [15, 16], which are adapted from the work described by T. Yokoi *et al.* [17].

The required materials, chemicals and reagents have been used as laboratory based. In preparation, the 20 mmol of dicarboxylic as succinic acid ($\text{HOOC}(\text{CH}_2)_2\text{COOH}$); 99.5% is dissolved in 200 cm^3 of ultra pure water, where the pH of solution is about 5.5 with adding of ammonia solution (aqu. NH_3 soln.; 25%) in appropriate amount. The 16.0 mmol of calcium carbonate (CaCO_3 ; calcite) has been suspended in the dicarboxylic acid solution and phosphoric acid (H_3PO_4 ; 85% aqu. soln.) 10.0 mmol is mixed with the suspension. Then suspension is stirred at 60°C , after about 3h, the pH of the suspension is reduced 5.5 to 5.0 by using of $1.0 \text{ mol. dm}^{-3} \text{ HCl}$ solution and after 30 minutes, the precipitates has been vacuum filtrated for isolation and rinsed with ultra pure water and ethanol ($\text{C}_2\text{H}_5\text{OH}$), followed by drying overnight at 40°C . The sample which synthesized in solution containing 20 mmol of succinic acid is denoted as Suc-20 as well as OCP those not containing dicarboxylate ion is synthesized also by using of CaCO_3 (16.0 mmol) and H_3PO_4 (12.0 mmol) which may denoted as CALPHOS. Now, CALPHOS(0.10g) and Suc-20(0.10g) are added to a 28-cm^3 teflon vessel with 10cm^3 of ultra pure water. The samples have incorporated as using of an autoclave, further by hydrothermally treatment at 180°C for 3h. In completion of phase transformation under hydrothermal treatment condition there are changing in morphology of generated HAP, if reaction time become longer due to aging, where hydrothermally treated sample has collected by vacuum filtration and it dried overnight at 40°C , respectively.

3. Results and Discussion

As we mentioned earlier that, the succinate incorporated OCP has been reported herein following a procedure well reported [15]. The report reveals that the molar ratio (Ca/P) of OCP with complexated succinate (Suc-OCP) ion is expected to be 1.56 ± 0.02 . The transformation of Suc-20 have proceeded under hydrothermal condition and Suc-OCP is transformed to HAP completely at 180°C for 3h by hydrothermal treatment. There is no by-products such as dicalcium phosphate anhydrous are detected by XRD analysis. It is reported that the colour changing of Suc-OCP from white to brown light upon the heating at 450°C in an air due to residual carbon formation. Notable, the colour of both CALPHOS & Suc-20 in visually, hydrothermal treatment is whitish and observed that non of the colour, which show under the before and after hydrothermal condition the decomposition of succinate ion may not occur.

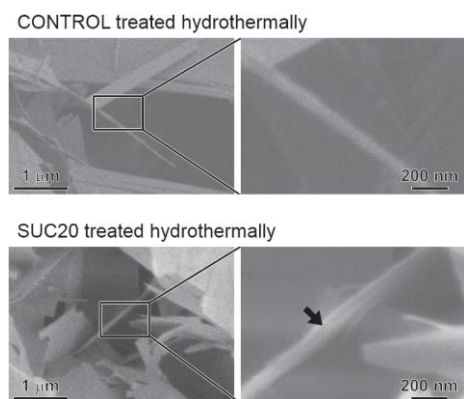
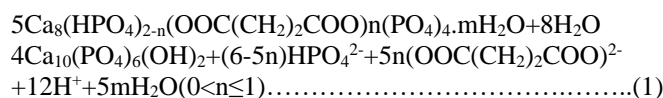


Fig 2: SEM magnification images of CONTROL or CALPHOS and SUC-20 (T. Yokoi *et al.*) under by hydrothermally treatment at 180°C for 3hr, where arrow indicate a dark line at center of HAP nanocrystal system.

Hydrothermally treatment at 180°C to 3h for samples (CONTROL or CALPHOS, Suc-20, Suc-OCP and Pure-OCP) the crystal morphology have been well assigned [16, 18]. Where the characterization of different products samples of crystalline phases are now being by scanning electron microscopy (SEM) and X-ray diffraction (XRD), and FTIR instrumentation. Figure 2, are showing the SEM magnification images of both samples as of CONTROL (CALPHOS) and Suc-20 under hydrothermal situation, which indicating dark line at center of sample crystals. The SEM and crystallite size calculation also supports the presence of dark line (S- line) corresponding to gap between to thin-plate crystals, therefore, the HAP crystal which are obtained from Suc-20 likely have laminated nanostructures. Where, the succinate ion elimination from OCP crystal interlayers may necessary for transformation of HAP from OCP with succinate ion encapsulation. Probably, the formation of laminated nanostructured due to in thickness direction the succinate ion to inhibit crystal growth. In XRD study, the absorption peak of HPO_4^{2-} located in the hydrated layer is detected at 1193cm^{-1} . This peak is not absorbed for Suc-20 because HPO_4^{2-} have replacement by succinate ion. The arising of observed peaks from the CH_2 bending modes and COO stretching of the incorporated succinate ion are observed at 1565 , 1460 and 1300 cm^{-1} . The absorption peak after hydrothermal treatment may corresponding to HAP are detected for both hydrothermally treated CALPHOS and Suc-20. Although, HAP crystalline lattice includes carbonate ions in hydrothermally synthesis in our samples, no detected absorption peak found in corresponding of carbonate ion. In crystalline phase terms the spectral observation of FTIR being in line of XRD results.



Showing, equation 1 the Suc-OCP transformation in hexagonal HAP is to be proceeded from the reaction. For samples, the crystal morphology before and after hydrothermal treatment at 180°C for 3h have displayed that, the both hydrothermally and synthesized show that the CALPHOS sample composed by plate-shaped crystalline in micrometer in size, where there crystalline phases is changed from OCP to HAP. Thus, the crystal morphology of pure-OCP, are almost retained after phase transformation [11, 12]. Similarly, to CALPHOS in macroscopic morphology there are no changing for Suc-20. These finding suggestion that for Suc-OCP transformation mechanism has similarity to that pure-OCP. On the basis of SEM images report of the different samples we observed that, the HAP crystals, where the thickness of crystalline HAP which is hydrothermally formed by treatment of CALPHOS is in range 50 - 150nm, having similarity to plate-shaped crystals hydrothermally (before) treatment. The present observation have shown the dark line (S- line) are found at the centre of the Suc-20 crystal after hydrothermal treatment, in other words, in preparation of HAP crystals from OCP encapsulated to succinate ion mostly has composed of laminated crystalline thin plate-shaped which can attribute as gapping between two different thin plate-shaped crystals and ought to be thinner than the HAP crystal generated from pure-OCP.

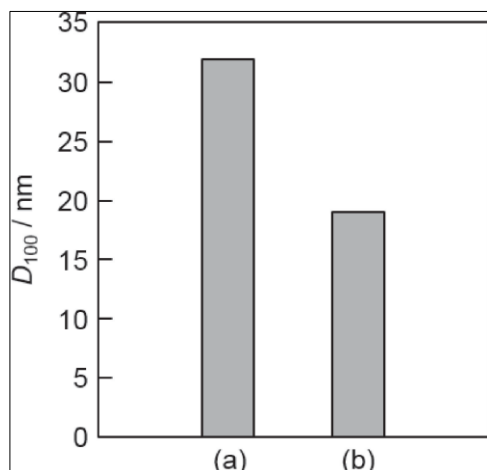


Fig 3: The D_{100} values of hydroxyapatite (HAP) prepared from, (a) CALPHOS, and, (b) Suc-20, calculated by using of Scherrer equation [$D_{100} = K\lambda/(\beta \cos\theta)$].

Since, in hexagonal HAP crystal system where the crystallite size in the direction of the various axes (a,b,c) dependent on plate-shaped HAP crystals thicknesses [12, 17, 19]. The size of crystals is perpendicular as to (100) plane, which are calculated by the using of Scherrer equation as given in eq. 2.

$$D_{100} = K\lambda/(\beta \cos\theta) \dots \dots \dots [2]$$

Where, D_{100} = the crystallite size perpendicular to (100) plane, K = Scherrer constant (=0.9), λ is the wavelength of incident X-ray (0.154 nm), β = the full width at half-maximum of the 100 peak of reflection for HAP & θ = the diffraction angle. The figure 3 have indicated the D_{100} values of both samples as HAP prepared from Suc-20 have smaller than that of HAP crystals which are synthesized from CALPHOS.

4. Conclusion

In the present articles, we have reported the scanning electron microscopy (SEM) images of transformed samples as the octacalcium phosphate (OCP) transformation with complexated succinate ion to laminated thin plate-shaped hydroxyapatite (HAP) under hydrothermal condition. The organically (succinate) modified plate-shaped OCP is transformed to pure-OCP and Suc-OCP in hydroxyapatite (HAP) under described condition at 180°C for 3h with adjusted pH to 5.5, where incorporated succinate ion having Ca/P molar ratio expected to be 1.56±0.02. The crystallite HAP mostly consisted to thin plate-shaped laminated nanocrystals with sub micrometer thicknesses. In characterization of transformed OCP to laminated thin HAP crystals the various technique such as SEM image and X-ray patterns have also been reported. The study of magnifying SEM images of samples CALPHOS or CONTROL and Suc-20, where the dark line at the center of the Suc-20 crystals have been observed, which can attributed to the gap between two thin plate crystals with indicating of its transformation from OCP to HAP.

5. References

1. Mishra SP. Int. J Scientific and Research Publications, 10,292,(2020); Chem. Sci. Int. J 2020;29:22-28.
2. Cotton FA, Wilkinson G, Murillo CA, Bochmann M. Adv. Inorg. Chem., Johnwelly & sons, Inc., 6th Edn., P413, 1999.

3. Dorozhkin SV, Epple M. Angew Chem., Int. Ed 2002;41:3130.
4. Mageed FAR, Kareem MM, Al-Baiati MN, Asian J Chem 2019;31:569.
5. Nguyen TT, Huynh CK, Le VT, Truong MD, Giang BL, Tran NQ *et al.* Asian J Chem 2019;31:1062.
6. Crane NJ, Popescu V, Morris MD, Steenhuis P, Igelzi MA. Jr., Bone 2006;39:434.
7. Horvathova R, Muller L, Helebrant A, Greil P, Muller FA. Mater. Sci. Eng. C 2008;28:1414.
8. Suzuki O, Imaizumi H, Kamakura S, Katagiri T, Curr. Med. Chem 2008;15:305.
9. Ioku K, Kawachi G, Sasaki S, Fujimori H, Goto S, Mater J Sci 2006;41:1341.
10. Goto T, Kim IY, Kikuta K, Ohtsuki C. J Ceram. Soc. Jpn 2012;120:131.
11. Kamitakahara M, Ito N, Murakami S, Watanabe N, Ioku K. J Ceram. Soc. Jpn 2009;117:385.
12. Ito N, Kamitakahara M, Murakami S, Watanabe N, Ioku K. J Ceram. Soc. Jpn 2010;118:762.
13. Yokoi T, Kato H, Kim IY, Kikuta IY, Kamitakahara M, Kawashita M, *et al.* Dalton Trans 2012;41:2732.
14. Yokoi T, Goto T, Kitaoka S. J Ceram. Soc. Jpn 2018;126:462.
15. Kamitakahara M, Okano H, Tanihara M, Ohtsuki C, Ceram J. Soc. Jpn 2008;116:481.
16. Yokoi T, Kato H, Kim IY, Kikuta K, Kawashita M, Ohtsuki C. Ceram. Int 2012;38:3815.
17. Yokoi T, Goto T, Kitaoka S, Chem. Lett 2019;48:855.
18. Koutsopoulos S, Biomed J. Mater. Res 2002;62:600.
19. Jhan J, Tseng YH, Chan JCC, Mou CY. Adv. Funct. Mater 2005;15:2005.