Phase Transformation of Organo-Modifided Plate-Shaped OCP to Laminated HAP Nanocrystals

Shiv Prakash Mishra

Assistant Professor in Chemistry (Guest Faculty)
Departmement of Physics & Electronics
Dr.Ram Manohar Lohiya Avadh University, Ayodhya-224001, (U.P.), India
E-mail: drspm9000@gmail.com

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Abstract: The formation of laminated thin plate-shaped hydroxyapatite (HAP) nanocrystals from organically modifided plate-shaped octacalcium phosphate (OCP) under hydrothermal condition which are performed at 180℃ for 3h with pH of solution adjusted to 5.5, further it incorporated succinate ion having Ca/P molar ratio is expected to be 1.56±0.02. The morphological observation of crystals have been characterized by XRD, SEM and other using patterns. Since, the HAP crystal system is hexagonally and its crystallite size in the direction of various (a,b,c) axes depending on the plate-shaped HAP crystals thickness, where their size as perpendicular to the (100) plane is calculated by using of Scherrer equation $D100 = K\lambda/(\beta \cos\theta)$.

Keywords: Hydroxyapatite, octacalcium phosphate, succinate ion .

[1]-INTRODUCTION:

Biologically, apatite are indispensable for which the general formula is $Ca_5(PO_4)_3X$, where X=F,Cl or OH, since they are key component of bone and teeth. Recently, synthetic apatites that permit bone grafts are now abailable[1].The hydroxyapatite (HAP,$Ca_{10}(PO_4)_6.(OH)_2$ which is the main inorganic components of hard tissue such as bone and teeth and they are used in medicinial application have attracted a great attention including several application such as artificial organs, tissue engineering, medical devices & dentistry etc[2,3]. Although ,fabricated biological hydrogels loaded biphasic calcium phosphate nanoparticles have also been reported for bone tissue regeneration[4]. Especially characteristics transformation behavious of octacalcium phosphate (OCP,$Ca_8(HPO_4)_2.(PO_4)_4.5H_2O$) to HAP have been reported, which has differences from other calcium phosphate compounds under hydrothermal conditions,(in *vitro* & *vivo*)[5-7]. The HAP may be prepared by various calcium orthophosphates such as α- & β-tricalcium phosphate (TCP,$Ca_3(PO_4)_2$) and OCP as well. For(α-,β-) TCP, because HAP is transformed by solvation pricipetation 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[8,9].

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[10,11]. Where, the hydrogen phosphate ion (HPO_4^{2-}) in the hydrated layres can be substituted or incorporated by dicarboxylate such as succinate ions into OCP crystal structure has been reported[12,13]. The molecular structure of succinic acid/ion is shown in figure -1.

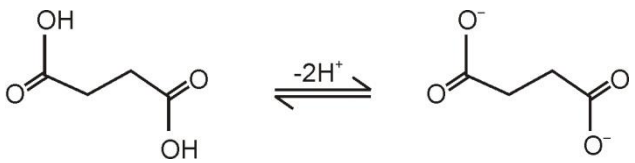

Figure 1. Structure of succinic acid ($HOOC.(CH_2)_2.COOH$) & its succinate ion $(OOC.(CH_2)_2.COO)^{2-}$.

[2]-EXPERIMENTAL :

The experimental procedure for organo-modified octacalcium phosphate (OCP,$(HPO_4)_2.(PO_4)_4.5H_2O$) with incorporated succinate ion has been synthesized by a previously reported method[14,15], which are adapted from the work described by T.Yokoi et al[16]. The required materials, chemicals/regents have been labotic bases standard, used. In preparation, the 20 mmol of dicorboxylic as succinic acid ($HOOC(CH_2)_2COOH$); 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 dicorboxylic 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℃, after about 3h, the pH of the suspension is reduced 5.5 to 5.0 by using of 1.0 mol. dm^{-3}HCl solution and after 30 minutes, the precipitates has been vacuum filtrated for isolation and rinsed with ultra pure water and ethanol(C_2H_5OH), followed by drying overnight at 40℃.

The sample which synthesized in solution containing 20 mmol of succinic acid is denoted as Suc-20 as well as OCP those not containing dicorboxylate 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℃ 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℃, respectively.

[3]- RESULTS & DISCUSSION :

As we mentioned earlier that, the succinate incorporated OCP has been reported herein following a procedure well reported[14]. 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℃ 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℃ in an air due to residual corbon 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.

Hydrothermally treatment at 180℃ to 3h for samples (CALPHOS, Suc-20 ,Suc-OCP & Pure-OCP) the crystal morphology have been well assigned[15,17]. Where the characterization of different products of crystalline phases are now being by X-ray diffraction (XRD), scanning electron microscopy (SEM) and other instrumentation. 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 complexated succinate ion are observed at 1565,1460 & 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 crystallic lattice includes corbonate ions in hydrothermally synthesis in our samples, no detected absorption peak found in corresponding of corbonate ion. In crystalline phase terms the spectral observation of FTIR being in line of XRD results.

$$5Ca_8(HPO_4)_{2-n}(OOC(CH_2)_2COO)n(PO_4)_4.mH_2O+8H_2O \longrightarrow$$

$$4Ca_{10}(PO_4)_6(OH)_2+(6-5n)HPO_4^{2-}+5n(OOC(CH_2)_2COO)^{2-}$$

$$+12H^{+}+5mH_2O \ (0 < n \leq 1) \qquad (1)$$

The HAP in Suc-OCP transformation is to proceeded from the reaction which are shown as above in eq. 1. For samples, the crystal morphology before & after hydrothermal treatment at 180℃ for 3h have displayed that, the both hydrothermally and synthesized show that the CALPHOS sample composed by plate-shaped crystallic in micrometer in size, where there crystallic phases is changed from OCP to HAP. Thus, the crystal morphology of pure-OCP, are almost retained after phase transformation[10,11]. 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 crystallic HAP which is hydrothermally formed by treatment of CALPHOS is in range 50 - 150nm, having similarity to plate-shaped crystals hydrothermally (before) treatment. The persent 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 crystallic thin plate-shaped which can attribute as gaping between two different thin plate-shaped crystals and ought to be thinner than the HAP crystal generated from pure-OCP.

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[11,16,18]. The size of crystals is perpendicular as to (100) plane, which are calculated by the using of

Scherrer equation (as eq.-2) with comparing HAP plate-shaped crystallite thickness of CALPHOS and Suc-20 after hydrothermal treatment at 180℃ for 3h.

$$D100 = K\lambda/(\beta \cos\theta) \quad \text{.....[2]}$$

Where, $D100$ = 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 $D100$ values of samples as HAP prepared from Suc-20 have smaller than that of HAP crystals which are synthesized from CALPHOS. 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.

[4]-CONCLUSION:

In the present articles, we have reported the synthesis and octacalcium phosphate (OCP) transformation with complexated succinate ion to laminated thin plate-shaped hydroxyapatite (HAP) under before and after 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℃ 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 submicrometer 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 well demonstrated to such study.

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