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Succinic acid and apatite world in producing thin plate-shaped Nanocrystals

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Abstract
Octacalcium phosphate (OCP) crystal is composed of apatite having general formula $Ca_5(PO_4)_3X$, where X=F, Cl or OH and they are key component of bone and teeth, where its hydrated layers producing thin plate-shaped hydroxyapatite (HAP) nanocrystals. Here, we have been reported the synthesis of sample of HAP nanocystals as CALPHOS or CONTROL and SUC or Suc-20 under hydrothermal condition from succinic acid's ion based OCP at 180 ^{0}C for 3hours. During incorporating of succinate ions in OCP crystals the hydrogen phosphate (HPO_4^{2-}) ions in the hydrated layers of OCP are being substituted by succinate ions. Since, HAP crystal system is hexagonal and it characterized by using of SEM, XRD and FTIR technique. The crystallite size of HAP crystals are as perpendicular to the (100) plane which can calculate by using as $D100 = K\lambda/(\beta \cos \theta)$ equation of Scherrer.

Keywords: Octacalcium phosphate, Hydroxyapatite, succinate ion

1. Introduction

In 'apatite world' where the 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, 2]. 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 and dentistry etc. [3, 4], as well as biphasic calcium phosphate (BCP) nanohydrogels for bone tissue regeneration [5]. Here, the characteristics transformation behaviours of octacalcium phosphate (OCP, $Ca_8(HPO_4)_2.(PO_4)_4.5H_2O$) to HAP and comparing from those of other calcium phosphate compounds which are prepared under hydrothermal conditions, (*in vitro* & *vivo*) [6-9] have reported. The HAP can be synthesized from various calcium orthophosphates such as α- and β- tricalcium phosphate (TCP,$Ca_3(PO_4)_2$) and OCP as well [10]. For TCP, since HAP is generated by a dissolution precipitation reaction, there is no correlation between the crystal shape of the original TCP particle and the shape of the HAP particles generated. Generally, needle shaped HAP crystals are formed from granular α- and β-TCP particles under hydrothermal conditions [11, 12].

In present article, we have been reported the succinic acid base octacalcium phosphate (OCP) transformation in hydroxyapatite (HAP) nanocrystals. Although, the octacalcium phosphate (OCP) crystal is composed of apatite and hydrated layers producing plate-shaped crystals have already reported [13, 14]. The hydrogen phosphate ion (HPO_4^{2-}) in the hydrated layres can be substituted or incorporated by succinate ions into OCP crystal structure has also been well reported [15-18]. The figure 1 is shown the molecular structure of succinic acid and succinate ion, respectively.

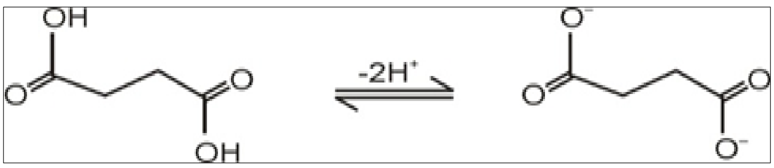

Fig 1: The structure of succinic acid ($HOOC.(CH_2)_2.COOH$) and its succinate ion ($(OOC.(CH_2)_2.COO)^{2-}$).

2. Experimental

In experimental, succinic acid-octacalcium phosphate (OCP; $(HPO_4)_2$. $(PO_4)_4$. $5H_2O$) as incorporated succinate ion has been synthesized by a previously reported method [19, 20], which are adapted from the work described by T. Yokoi *et al*. [21]. The required materials, chemicals and reagents have been laboratory base. Firstly, in this method, 20 mmol of succinic acid (HOOC $(CH_2)_2$COOH); 99.5%, (Wako Pure Chemical Industries Ltd., Osaka, Japan) is dissolved in 200 cm^3 of ultra pure water, where the pH of solution is adjusted to 5.5 by adding an appropriate amount of ammonia solution (aqu.NH_3 soln.; 25%). The 16.0 mmol of calcium carbonate ($CaCO_3$; calcite, Nacalai Tesque Inc., Kyoto, Japan) has been suspended in the dicorboxylic acid solution and 10.0 mmol of phosphoric acid (H_3PO_4; 85% aqu. soln., Wako Pure Chemical Industries Ltd) is mixed with the suspension. Then suspension is stirred at 60℃, after about 3h, the pH of the suspension is reduced to 5.0 by using 1.0 mol. dm^{-3}HCl solution and after 30 minutes, the precipitates has been isolated by vacuum filtration and gently 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 also synthesized by using 16.0 mmol of $CaCO_3$ and 12.0 mmol of H_3PO_4 which may denoted as CONTROL or CALPHOS. Now, CALPHOS (0.10g) and Suc-20(0.10g) are added to a 28-cm^3 Teflon vessel with 10cm^3 of ultrapure water. The samples have encapsulated in an autoclave, and then hydrothermally treated at 180 ℃ for 3h. These hydrothermal treatment condition under which the phase transformation is completed in a short time may selected because as the reaction time become longer, the morphological differences in the morphology of generated hexagonal HAP due to different starting materials disappear due to aging, where hydrothermally treated sample has collected by vacuum filtration and it dried overnight at 40 ℃, respectively.

The crystalline phases of the different hydroxyapatite (CALPHOS or CONTROL and Suc- or SUC 20) sample products have characterized by powder X-ray diffraction (XRD; RINT-2000, Rigaku Co., Tokyo, Japan) using Cu-Kα radiation. The chemical structures of the given samples have characterized by using of Fourier- transform infrared (FTIR) spectroscopy (Frontier MIR/NIR, Perkin-Elmer Japan Co., Ltd., Kanagawa, Japan) as using the KBr tablet method. The morphologies of the formed samples have been characterized by scanning electron microscopy (SEM; SU-8000, Hitachi, Ltd., Tokyo, Japan).

3. Results and Discussion

Here, we have effort to study of synthesis and characterization of succinate ion based OCP to HAP, although, following a procedure well reported [19]. The report reveals that the Ca/P molar ratio of pure OCP with incorporated succinate (SUC- or Suc-OCP) ion is expected to be 1.56± 0.02. From pure OCP, the transformation of Suc-20 have proceeded under hydrothermal condition where Suc-OCP is completely transformed to HAP by hydrothermal treatment at 180℃ for 3h. There is no by- products such as dicalcium phosphate anhydrous are detected by XRD analysis. It is reported that the colour of Suc-OCP changed from white to light brown upon heat treatment at 450℃ in an air due to residual corbon formation. Notable, the colour of both CONTROL or CALPHOS and Suc-20 before and after hydrothermal treatment was white and non of the colour may observed visually. Hence succinate ion decomposition may not occur under the hydrothermal conditions.

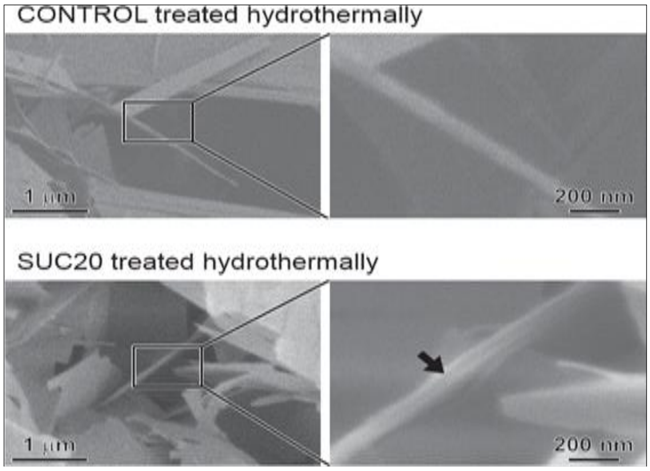

Fig 2: SEM magnification images of samples CONTROL or CALPHOS and SUC-20 (T. Yokoi *et al.*) under by hydrothermally treatment at 180 ^{0}C for 3hr, where the black arrow indicates a dark line at center of HAP nanocrystal system

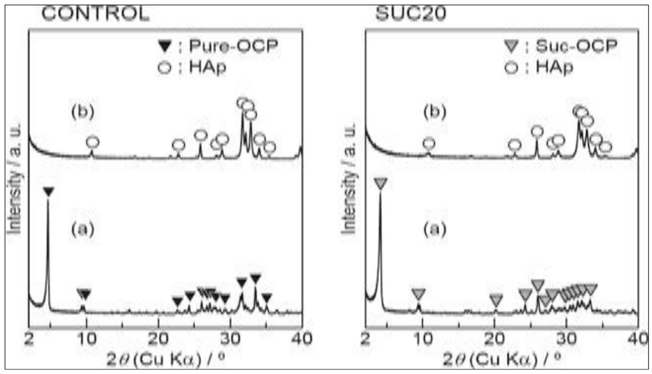

Fig 3: The XRD patterns of samples CONTROL and SUC20 under {before (a), and after (b)} hydrothermal treatment at 180 °C for 3 hour

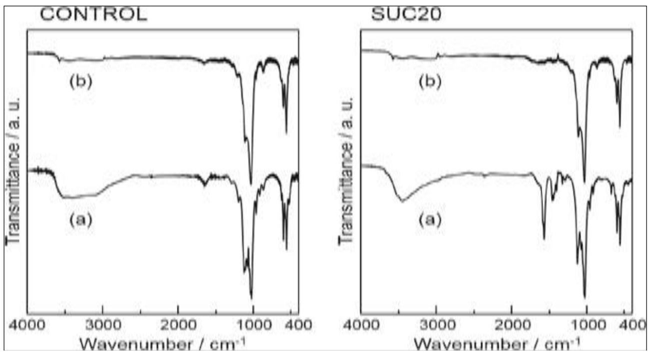

Fig 4: The FTIR spectra of samples CONTROL and SUC20 under {before (a), and after (b)} hydrothermal treatment at 180 °C for 3 hour

Although, crystal morphology of the OCP samples as CALPHOS or CONTROL, Suc-20, Suc-OCP and Pure-OCP under hydrothermal treatment at 180 ℃ for 3h have been well assigned [20, 22]. The figure 2 have shown the scanning electron microscopy (SEM) observation of dark line at HAP crystal's center and the crystalline phases of the different products are being characterized by powder X-ray diffraction (XRD) as in figure 3. The figure 4 indicated FTIR spectra with the absorption peak of HPO_4^{2-} located in the hydrated layer is detected at 1193cm^{-1}, [23]. This peak is not absorbed for Suc-

20 because HPO_4^{2-} is replaced by the succinate ion. The observation peaks arising from the COO stretching and CH_2 bending modes of the complexated succinate ion are observed at 1565, 1460 and 1300 cm^{-1}. After the hydrothermal treatment, the absorption peak corresponding to HAP are detected for both hydrothermally treated CALPHOS and Suc-20. Although, in some cases, hydrothermally synthesized HAP includes corbonate ions in its crystal lattice, the absorption peaks corresponding to the corbonate ion are not detected in our samples. In crystalline phase terms the FTIR spectral observation are in line with XRD results. The transformation from Suc-OCP to hexagonal HAP is proposed to proceed from the reaction which are shown as above in eqation 1.

$5Ca_8(HPO_4)_{2-n}(OOC(CH_2)_2COO)n(PO_4)_4.mH_2O+8H_2O$
$4Ca_{10}(PO_4)_6(OH)_2+(6-5n)HPO_4^{2-}+5n(OOC(CH_2)_2COO)^{2-}$
$+12H^++5mH_2O$ $(0< n \leq 1)$……………………………….... (1)

In crystal morphology of the samples under hydrothermal treatment at 180℃ for 3h have displayed that, both the as-synthesized and hydrothermally treated CALPHOS sample are composed of plate-shaped crystals several micrometers in size, although the crystalline phase is changed from OCP to hexagonal HAP. Therefore, for pure-OCP, the crystal morphology is almost retained after phase transformation [13, 14]. Similarly, to CALPHOS there is no change in the macroscopic morphology for Suc-20. These finding strongly suggested that the phase transformation mechanism for Suc-OCP is similar to that of pure- OCP. On the basis of SEM images report of the different samples we observed that, the HAP crystals, where the thickness of HAP crystals, formed by the hydrothermal treatment of CALPHOS is in range 50 - 150nm similar to those of plate-shaped crystals before hydrothermal treatment. The present observation have shown the dark line (S-line) are found at the centre of the Suc-20 crystal after hydrothermal treatment, which can attributed to the gap between two thin-plate crystals. In other words, the hexagonal HAP crystal synthesized from OCP with incorporated succinate ion is likely composed of laminated thin plate-shaped crystals and ought to be thinner than the HAP crystal generated from pure-OCP.

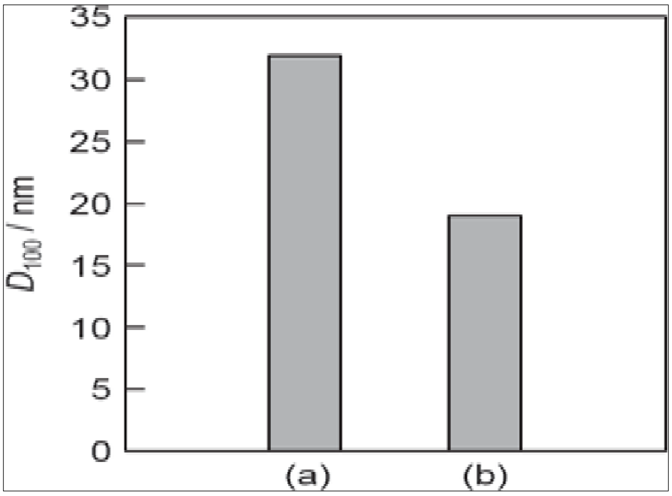

Fig 5: The D_{100} values of hydroxyapatite (HAP) prepared from, (a) CALPHOS and (b) Suc-20, calculated by using of Scherrer equation

A hydroxyapatite, HAP crystal system is hexagonal, where the crystallite size in the direction of the various axes (a,b,c) which dependent on the thickness of the plate-shaped HAP crystal [14, 21, 24, 25]. The crystallite size perpendicular to the (100) plane which are calculated by the using of Scherrer equation (eq.-2) to compare the thickness of the plate-shaped HAP crystal of CALPHOS and Suc-20 after hydrothermal treatment at 180℃ for 3hours. Figure 5 show that the $D100$ values of samples as HAP synthesized from Suc-20 are smaller than those of HAP prepared from CALPHOS. Thus, calculation of crystallite size support as well as SEM agreement that, 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 elimination of succinate ion from interlayer of OCP crystal is necessary for the transformation from OCP with incorporated succinate ion to HAP. The laminated nanostructure is formed probably because the succinate ions inhibit crystal growth in the thickness direction.

$D100 = K\lambda / (\beta \cos\theta)$ ……………………….……………. [2]

Where, $D100$ is the crystallite size perpendicular to (100) plane, K is Scherrer constant (=0.9), λ is the wavelength of incident X-ray (0.154 nm), β is the full width at half-maximum of the 100 reflection peak for HAP and θ is the diffraction angle

4. Conclusion

In conclusion, we have reported the succinic acid and their complexate with apatite as octacalcium phosphate (OCP), which is key components of bone and teeth. Where the hydrated layers of apatite OCP is transformed and producing a thin plate-shaped hexagonal hydroxyapatite (HAP) nanocrystals. These are transformed through hydrothermal precipitation reaction at 180℃ for 3h. During incorporation of succinate ions into OCP crystal the substitution of hydrogen phosphate (HPO_4^{2-}) ions in hydrated layer of OCP are replaced by succinate ions. The generated samples of HAP crystals from OCP is characterized by using SEM, X-ray diffraction and FTIR. Crystalline size and thickness of samples can be calculated by introducing of Scherrer equation as $D100 = K\lambda/(\beta \cos\theta)$, where, $D100$ values of the sample are smaller than the thickness of the thin plate crystals as observed by SEM.

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