Enhanced reactivity of dicalcium phosphate dihydrate with fluoride ions by coating with apatite nanoparticles

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\textbf{ABSTRACT}

The formation of nanoscale precursors on the surface of dicalcium phosphate dihydrate (DCPD) is an important step in various methods; however, this process requires an unstable solution. Herein, we propose a simple method for the deposition of nanoscale fluorapatite (FAp) particles on the surface of DCPD particles using a weakly acidic, aqueous solution containing only calcium, phosphate, and fluoride ions ([CaF\textsubscript{2}]\textsubscript{0.5}P\textsubscript{2}O\textsubscript{7})\textsubscript{0.5}(OH)\textsubscript{3}. Repeated immersion in the same solution increases the amount of FAp deposition and almost no delay time is observed. Experimental results indicate that approximately 10 wt.% of FAp on the DCPD surface is optimal to enhance its reactivity with fluoride ions. Our results demonstrate an optimum FAp deposition amount on DCPD particles for improved reactivity with fluoride ions, and we achieved an improved surface of the DCPD particle for fluoride immobilization in wastewater and soil environments.

\textbf{1. Introduction}

Calcium phosphates are promising materials for various clinical applications because of their desirable biocompatibilities. In aqueous solutions, calcium phosphates are converted to another form with a lower solubility. This conversion reaction is observed in various applications, such as during the self-setting of calcium phosphate cement, which comprises calcium phosphate and other chemicals [1]. It also takes place when applying acidic fluoride solutions to dental enamel surfaces to prevent dental caries [2]. Inorganic dental enamel consists of hydroxyapatite (HAp, Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}(OH)\textsubscript{2}), which transforms into dicalcium phosphate dihydrate (DCPD, CaHPO\textsubscript{4}2H\textsubscript{2}O) under acidic conditions [3]. The more stable fluorapatite (FAp, Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}F\textsubscript{2}) can then form via a reaction between the DCPD intermediate and fluoride ions [4,5]. Our research group investigated the use of this conversion of DCPD to FAp for the removal of fluoride ions in a water environment.

Fluoride pollution is an important environmental issue because of its harmful effects on human health. In particular, fluoride pollution of water (such as groundwater) is a serious environmental problem [6]. Approximately 30 countries encounter fluoride pollution in drinking water, which can lead to dental and skeletal diseases such as dental fluorosis [7]. Among the various fluoride salts, FAp has a relatively low solubility and is distributed as stable natural rocks, such as phosphorous rock. Stabilizing the fluoride ions in water by converting them to FAp using DCPD is one of many methods for the remediation of fluoride-polluted water. Previously, DCPD was used to stabilize fluoride in aqueous solutions, where it was determined that DCPD is beneficial for stabilizing fluoride ions in water [8] and phosphogypsum in industrial waste [9]. However, the reaction of DCPD with fluoride ions is affected by coexisting ions, such as magnesium ions [10].

We also investigated the mechanism behind DCPD reacting with fluoride ions and found that DCPD did not directly react with fluoride ions; instead, a nanoscale precursor particle that formed on the DCPD surface during the initial stage reacted with the fluoride ions. This formation required a few hours, after which the fluoride ions rapidly reacted with the precursor to form FAp [11]. The precursor consisted of HAp-like calcium phosphate that could be easily deposited onto the DCPD surface by mixing it with warm water [12]. The HAp on the DCPD surface was then converted into FAp using fluoride ions, and the FAp particles were grown by employing calcium and phosphate ions in DCPD and fluoride ions in the solution. Coexisting ions, such as cadmium [13], magnesium [14], and fluoride ions [15], inhibit the deposition of the precursor onto the DCPD particles and hamper its reactivity with fluoride ions. Based on these results, the deposition of the nanoscale precursor on the DCPD...
particles is beneficial for improving the reactivity of DCPD. After the DCPD reaction, the obtained FAp particles have an identical morphology to that of the initial DCPD [11]. These phenomena are useful for wastewater treatment because the particle size of FAp after wastewater treatment using DCPD is larger than that of the particles obtained via conventional treatment processes. Moreover, the addition of flocculants is not required, leading to a decrease in the sludge volume. Therefore, the use of DCPD is beneficial to water treatment because of the elimination of the need for chemical additives, the reduction in the amount of sludge, and the lowering of operational costs [16].

Prior investigations revealed that the mixing of HAp with DCPD was also effective in improving the reactivity with fluoride ions; however, the particle morphology resembled that of HAp, rather than DCPD [17]. Based on these findings, the deposition of nanoscale precursors onto the surface of DCPD particles is an important methodology for various applications. Considering the aforementioned reaction mechanism, both HAp and FAp are suitable for serving as the nanoscale precursor.

In our previous reports, the deposition of HAp nanoparticles was achieved by immersing DCPD in simulated body fluid (SBF) [18], which has similar concentrations of inorganic ions to human body plasma and is widely used for the HAp coating of various materials in the field of biomaterials [19]. The concentrations of calcium and phosphate ions in SBF are supersaturated for the HAp coating, meaning that SBF is an unstable solution. The preparation and storage of SBF require sensitive techniques, and fluoride ions cannot be added to the original composition. In previous reports regarding coating of an apatite layer on the artificial peptide using fluoride-containing SBF (s-SBF) [20], the pH of the s-SBF was adjusted to 6.8, which involved a slight shift toward acidic conditions from the original SBF (pH 7.40).

Herein, novel methods employing a simple and stable solution for the deposition of HAp or FAp nanoparticles onto the surfaces of DCPD particles are investigated. In some studies, the solution composition for coating the material surface with HAp comprises calcium and phosphate [21]. However, this type of solution is unstable because the pH value is approximately 7.4 at 309.5 K, which is equal to that of human body plasma. The solubility of calcium phosphates, including DCPD, HAp, and FAp, depends on the pH of the aqueous solution and increases with a decrease in the pH value [22]. When DCPD is mixed with water, the solution pH shifts toward neutral pH, owing to the hydrolysis of phosphate ions generated from DCPD [8,9]. Using this phenomenon, HAp or FAp is introduced onto the surface of DCPD particles from an acidic solution containing calcium and phosphate ions.

In this study, we investigated the effects of the pH and composition of the treatment solution on the deposition of nanoscale precursor particles on DCPD particle surfaces. The effects of surface modification on the reactivity of DCPD with fluoride ions were also evaluated.

2. Materials and methods

2.1. Materials

Reagent grade DCPD (Yoneyama Chemical Industry Co., Ltd., Osaka, Japan) was used as the starting material. Fluoride solutions were prepared by mixing NaF in water. The NaF and other chemicals were of reagent grade (FUJIFILM Wako Pure Chemical Corp., Osaka, Japan). Water was purified via ion exchange and ultrafiltration (Milli-Q A10, Merck-Millipore, Burlington, MA, USA).

Two types of solution were used for surface modification and their chemical compositions are presented in Table 1. One solution contains calcium and phosphate ions (C-P solution), and the other contains calcium, phosphate, and fluoride ions (C-P-F solution). The calcium and phosphate concentrations of the C-P and C-P-F solutions were adjusted to the corresponding values of SBF (1.0 and 2.5 mmol/L, respectively). The concentration of fluorides in the C-P-F solution was 1.58 mmol/L (30 mg/L). Sodium hydroxide and hydrochloric acid were used to adjust the pH of each solution.

2.2. Methods

2.2.1. Change of pH by addition of DCPD

To determine the optimal pH values of the C-P and C-P-F solutions, changes in the pH upon the addition of DCPD were measured. The pH of 20 mL of the C-P or C-P-F solution was adjusted to different pH values and mixed with 1 g of DCPD in a polyethylene terephthalate centrifugation tube. The mixture was shaken for 24 h using a reciprocal shaker (NR-1, TAITEC Corporation, Saitama, Japan). The shaking speed was set to 80 rpm and the temperature was adjusted to 298 K. The liquid phase was separated via pressure filtration through a cartridge membrane filter (pore size: 0.45 μm) and the pH value of the liquid phase was analyzed using a pH electrode (InLab Expert Pro,

| Table 1 | Concentrations of inorganic ions in C-P and C-P-F solutions compared to those in simulated body fluid (SBF). |
|----------------------------------|
| **Ion Concentrations (mmol/L)** |
| **Solution** | Na\(^+\) | K\(^+\) | Mg\(^2+\) | Ca\(^2+\) | Cl\(^−\) | HCO\(_3\)\(^−\) | HPO\(_4\)\(^2−\) | SO\(_4\)\(^2−\) | F\(^−\) |
| SBF | 142 | 5 | 1.5 | 2.5 | 148.8 | 4.2 | 1 | 0.5 | - |
| C-P | - | - | 2.5 | - | - | - | 1 | 1.6 | - |
| C-P-F | - | - | 2.5 | - | - | 1 | - | - | - |
Mettler Toledo, Columbus, OH, USA) connected to a pH/ion meter (Seven Compact, Mettler-Toledo).

### 2.2.2. Surface modification of DCPD particles

The surface modification of the DCPD particles was carried out by soaking 1 g of DCPD powder in 50 mL of the C-P or C-P-F solution. The mixture was shaken for 24 h under the same conditions described in the previous section. The treated DCPD was separated via vacuum filtration using a membrane filter (pore size: 0.45 μm) and dried in a convection oven at 313 K. The obtained crystalline solid phases were analyzed via powder X-ray diffraction (XRD, MiniFlex, Rigaku Corporation, Tokyo, Japan) employing CuKα radiation. The surface morphologies and atomic compositions were analyzed via scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS, JSM-6390AX, JEOL, Ltd., Tokyo, Japan) and scanning ion microscope (SIM, JIB-4000, JEOL, Ltd., Tokyo, Japan) using gallium ion. To determine its calcium and phosphorus contents, the solid phase was dissolved in nitric acid. The calcium and phosphorus concentrations of the obtained solutions were determined using inductively coupled plasma optical emission spectrometry (ICP-OES, 720ES, Agilent Technologies, Inc., Santa Clara, CA, USA) with argon plasma.

### 2.2.3. Reactivity toward fluoride ions

As reported in a previous study [11], the reaction of DCPD with fluoride ions requires several hours, after which the fluoride concentration in the solution decreases rapidly. To observe this process, the fluoride concentration in the solution after mixing with DCPD was continuously monitored. Figure 1 shows a schematic of the experimental apparatus. Three hundred milliliters of fluoride solution, containing 20 mg/L of fluoride prepared from sodium fluoride and 0.3 g of DCPD samples, was placed in a baffled glass reactor. These were mixed with a propeller at 200 rpm, and the fluoride concentration of the solution was continuously monitored using an ion-selective electrode (ISE, ORION 9606BNC, Thermo-Fisher Scientific, Waltham, MA, USA) and a pH/ion meter. After treatment for 24 h, the solid phase was separated using vacuum filtration and subjected to powder XRD and SEM. Additionally, 0.02 g of DCPD was mixed with 20 mL of a 20 mg/L fluoride solution and stirred for different time periods. The amount of fluoride ions removed by DCPD was calculated by the change in fluoride concentration before and after the reaction.

### 3. Results and discussion

#### 3.1. Optimum pH of treatment solution

The optimum pH values of the C-P and C-P-F solutions were determined by changing the pH value via DCPD addition. Figure 2 shows the pH values before and after the addition of DCPD, where we observed that the pH values of the C-P and C-P-F solutions after DCPD addition remained constant when their initial pH values were 4–7 and 3–7, respectively. In a prior study, it was determined that the pH of water shifted toward a neutral pH value upon DCPD addition because low amounts of DCPD dissolved and released phosphate ions that acted as a buffer [8]. For the C-P or C-P-F solutions, the pH value after DCPD addition was lower than that of the water sample. The solubility of
DCPD increases under acidic conditions. Additionally, a solution containing calcium and phosphate ions is unstable and easily forms a precipitate at neutral pH. Therefore, the optimum pH value of the C-P and C-P-F solutions is approximately 4.5.

3.2. Effect of fluoride ions in the solution on DCPD surface modification

The effect of fluoride ions in the solution on the deposition of HAp or FAp particles on the surfaces of DCPD particles was investigated by reacting DCPD with the C-P and C-P-F solutions.

Figure 3 shows the powder XRD patterns of the solid phase after the separate reactions of DCPD with the C-P and C-P-F solutions for one day. The solid phase obtained after these reactions was analyzed using SEM and EDS (Figure 4). HAp was expected to precipitate on the surfaces of the DCPD particles when the C-P solution was used; however, no HAp diffraction peaks were observed in the powder XRD pattern of DCPD after its reaction with the C-P solution (Figure 3). As shown in Figure 4, the surfaces of the DCPD particles after the reaction are as smooth as the surface of DCPD before the reaction, indicating no deposition of particles. In contrast, small diffraction peaks, which may correspond to either HAp or Fap, are observed in the data for DCPD after its reaction with the C-P-F solution (Figure 3). The SEM results shown in Figure 4 indicate that small particles formed on the surfaces of the DCPD particles. Furthermore, the EDS data show that the fine particles consist of calcium, phosphate, and fluorine. Figure 5 shows a higher-magnification SIM photograph of the surface of the DCPD particle treated with the C-P-F solution. The small particles formed on the surface of the DCPD have a needlelike morphology, in contrast with the reptile shape that is the characteristic morphology of HAp. This needlelike shape has previously been observed in fluoridated apatites [23], and in FAp obtained from DCPD [11]. These results confirm that FAp is formed in the solid phase and that fine FAp particles form on the DCPD particle surfaces.

Figure 4. Scanning electron microscopy (SEM) images of the DCPD surface treated with the C-P and C-P-F solutions and energy dispersive X-ray spectroscopy (EDS) data of DCPD treated with C-P-F solution. The pH value of the solutions is 4.5.
To understand the difference in the induction of apatite particles on the DCPD particle surface by the C-P and C-P-F solutions, we discuss here the effect of the change in the supersaturation of these solutions due to the change of the pH value with the addition of the DCPD into the solutions. The supersaturation (S) of HAp and FAp in an aqueous solution can be described as the ratio of the ionic product (IP) and solubility product (Ksp) [24,25] that are calculated from the ionic concentrations according to equations (1) to (3):

\[
S = \frac{IP}{Ksp}
\]  

(1)

For HAp,

\[
IP = [Ca^{2+}]^{10}[PO_{4}^{3-}]^{6}[OH^{-}]^{2}
\]  

(2)

\[
Ksp = 5.5 \times 10^{-118}
\]

And for FAp,

\[
IP = [Ca^{2+}]^{10}[PO_{4}^{3-}]^{6}[F^{-}]^{2}
\]  

(3)

\[
Ksp = 5.0 \times 10^{-123}
\]

Because the concentrations of the PO\(_{4}^{3-}\) and F\(^{-}\) ions depend on the pH of the solution according to equations (4) and (5), IP and S are changed by the pH of the solution.

\[
H_{3}PO_{4} \rightleftharpoons H_{2}PO_{4}^{-} + H^{+} \rightleftharpoons HPO_{4}^{2-} + 2H^{+} \rightleftharpoons PO_{4}^{3-} + 3H^{+}
\]  

(4)

\[
HF = F^{-} + H^{+}
\]  

(5)

Based on these prerequisites, the changes in the IP value of HAp and FAp in the C-P and C-P-F solutions against the pH value are shown in Figure 6. This figure shows the conditions under which the IP values of each solution exceed the Ksp values for HAp and FAp, as an indication of the supersaturation of the solutions. The supersaturation of the C-P-F solution for FAp was larger than that of the C-P solution for HAp. This difference seems to lead to the difference in the phenomena of apatite deposition on the DCPD surface occurring with these two solutions.

The reactivity of fluoride ions with DCPD after its treatment with the C-P and C-P-F solutions was investigated using batch experiments (described in the last section of Materials and Methods). Figure 7 shows the change in the fluoride ion concentration with the addition of DCPD after treatment with the C-P and C-P-F solutions. The time period for the reaction of DCPD with the fluoride ions did not change after its treatment with the C-P solution, but it did decrease upon its treatment with the C-P-F solution.

Figures 8 and 9 display the powder XRD patterns and SEM images of DCPD after its reaction with fluoride ions for 24 h. All DCPD samples were transformed into FAp-modified samples but retained the DCPD morphology. These results show that DCPD treatment with the C-P-F solution increases the reactivity of DCPD with fluoride ions without affecting the reaction characteristics. Furthermore, the results indicate that FAp can form on the DCPD particle surfaces without disrupting the original DCPD morphology. Therefore, treatment of DCPD with the C-P-F solution increases its reactivity with fluoride ions through the deposition of nanoscale FAp particles on the DCPD particle surface.
Figure 7. Changes in fluoride ion concentration of the fluoride solution after the addition of untreated DCPD and DCPD treated with the C-P and C-P-F solutions.

Figure 8. Powder XRD patterns of DCPD after reaction with fluoride ions.

3.3. Optimal FAp content for fluoride removal

In our previous study on the treatment of DCPD using SBF [18], the content of the HAp particles present on the DCPD particle surfaces was an important factor in the improvement of its reactivity with fluoride ions. The effect of the C-P-F solution treatment method on the amount of FAp deposited onto the DCPD particle was investigated to determine if this amount could be controlled.

To increase the amount of FAp deposition, 1 g of DCPD was added to 50 mL of C-P-F solution and shaken for 24 h. This immersion process was repeated with fresh amounts of C-P-F solution. Figure 10 shows the powder XRD patterns of DCPD after this repeated immersion, where an increase in the intensity of the FAp diffraction peaks was observed.

The solid phase obtained after two immersions in the C-P-F solution was evaluated via SEM (Figure 11), where the amount of FAp deposited had increased compared to that observed for the DCPD sample without repeated immersion. Therefore, fine FAp particles are deposited onto the surfaces of DCPD particles even after repeated immersion. As the number of repetitions increases, the amount of FAp deposition also increases. The FAp amount on the DCPD particle surfaces was calculated from the Ca/P molar ratio obtained via ICP-OES analysis of the DCPD dissolved in nitric acid. This method was used in our previous study to investigate the amount of HAp present on the DCPD particle surfaces [18].

Figure 12 shows the relationship between the amount of FAp in DCPD and the Ca/P ratio. The Ca/P ratio of stoichiometric FAp is 1.67; however, the obtained FAp is calcium-deficient, and the Ca/P ratio is approximately 1.53. The amount of FAp is depicted by a solid line in the figure.

Figure 13 shows the variation in the amount of FAp on the DCPD particles after repeated immersion, which successfully increased with an increasing number of immersions.

Different amounts of FAp on the DCPD particle surfaces were tested to determine the optimal amount for improving the DCPD reactivity with fluoride ions. The increase in FAp on the DCPD surface caused the amount of DCPD in the FAp/DCPD hybrid to decrease, which subsequently resulted in the removal of fluoride ions. As shown in Figure 7, if the induction period occurs during the reaction of DCPD with fluoride ions, the fluoride ions are removed very rapidly. Moreover, the amount of fluoride ions removed by the DCPD/FAp hybrid decreases with increasing FAp content because FAp cannot react with fluoride ions and instead acts as a precursor in the reaction of DCPD with fluoride ions. Based on these observations, the optimum amount of FAp hybridized on the DCPD particle surface is limited by the induction period and the amount of fluoride removed during the DCPD reaction. In our previous study, we suggested that the enhancement of the reaction could be evaluated by noting the amount of fluoride ions removed after 1 h of reaction [18]. The amount of fluoride ions removed by the DCPD/FAp hybrid can be determined by the variation in the fluoride ion concentration after 24 h of reaction. Figure 14 shows the amount of fluoride ions removed by DCPD/FAp hybrids with different FAp contents. The amounts of fluoride ions removed after 1 and 24 h of reaction are different when the FAp
contents are < 10 wt.%. This indicates that the induction period of DCPD with fluoride ions does not improve at these FAp contents. The amount of fluoride ions removed after 24 h of reaction decreases with an increase in the FAp content, which is consistent with the calculated value from the DCPD content of the hybrid, as depicted by the dotted line in Figure 14. Based on these results, 10 wt.% FAp hybridized on the DCPD particle surface is an appropriate amount to improve the induction period of the DCPD/FAp hybrid and the amount of fluoride it removes from the water environment.

4. Conclusion

In this study, the reactivity of DCPD with fluoride ions was enhanced by modifying the DCPD particle surface using a weakly acidic solution with a simple composition of only calcium, phosphate, and fluoride ions. The key points are summarized below.

(1) When DCPD is added to the C-P and C-P-F solutions, the post-reaction pH changes at pH < 4 in the case of the C-P solution, whereas it remains constant when the pH is between 4 and 7, regardless of the initial pH. In the case of the C-P-F solution, the post-reaction pH is constant between 3 and 7, regardless of the initial pH.

(2) The addition of DCPD to the C-P solution does not result in the deposition of HAp onto the DCPD surface.

(3) When DCPD is added to the C-P-F solution, a small amount of FAp is deposited onto the DCPD surface. Furthermore, the amount of FAp deposited increases as the number of repeated immersions in the solution increases.

(4) The reactivity of the product phase with fluoride ions does not increase in the C-P solution. However, the reactivity of the FAp/DCPD hybrid (obtained from the C-P-F solution) with fluoride ions increases, and the time of the induction period decreases. Repeated immersion in the same solution increases the amount of FAp deposition, and almost no delay time is observed. Finally, 10 wt.% FAp deposited onto the DCPD particle surface is
Figure 11. Effect of the repeated immersion on the surface morphology of DCPD particles after treatment with the C-P-F solution, observed by SEM.

Figure 12. Relationship between the molar ratio of calcium and phosphate ions (Ca/P ratio) and the FAp content in the DCPD/FAp hybrid.

Figure 13. Effect of repeated immersion on the FAp content of DCPD particles.

Figure 14. Amount of fluoride ions removed after 1-h (closed circle) and 24-h (open circle) reactions with DCPD/FAp hybrids containing different FAp amounts. The dotted line in the figure indicates the removed amount of fluoride ions, calculated from the change in fluoride concentration before and after the reaction.
the optimal amount to enhance the reactivity of DCPD with fluoride ions.

Our results determined an optimum amount of FAp to be deposited on the surface of DCPD particles, via a C-P-F solution, to improve the reactivity of DCPD with fluoride ions. The results of this study can be applied to the design of functional materials for the removal of fluoride ions from affected environments, such as wastewater and polluted soil.

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Disclosure statement

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