

## Morphology Changing at Incipient Crystallization Condition

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**Abstract.** Brushite (Dicalcium phosphate dihydrate, (DCPD),  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) is one of key components in calcium phosphate system due to wide attractive material not only as bioceramics but also environmental materials. Morphology of DCPD crystals is important factor when one uses its functionality with chemical reaction; because its surface crystal face, shape and size rule the chemical reactivity, responsiveness. Moreover, physical properties are also changed the morphology; such as cohesion, dispersiveness, permeability and so on. If one uses DCPD crystals as environmental renovation materials to catch the fluoride ions, their shape require 020 crystal surfaces; which usually restricts their shape as plate-like structure. After the chemical reaction, the shape of sludge is not good for handling due to their agglutinate property. Therefore searching an effective parameter and developing the method to control the morphology of DCPD crystals is required. In past, we reported that initial concentration and pH value of starting solution, prepared by dissolving calcium nitrate,  $\text{Ca}(\text{NO}_3)_2$  and ammonium dihydrogen phosphate,  $\text{NH}_4\text{H}_2\text{PO}_4$ , changes the morphology of DCPD crystals and phase diagram of morphology of DCPD crystal depend on those parameter. The DCPD crystallization shows unique behaviour; products obtained higher initial concentration form single crystal-like structure and under lower condition, they form agglomerate crystal-like structure. These results contradict usual crystallization. Here we report that the effect of mixing process of two solutions. The morphology of DCPD crystals is changed from plate structure to petal structure by the arrangement. Our result suggests that morphology of DCPD crystals strongly depends at incipient crystallization condition and growth form is controllable by setting initial crystallization condition.



## 1. Introduction

DCPD (dicalcium phosphate dihydrate,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ) crystal is one of key components in calcium phosphate system and used as a coating for orthopaedic implants, starting materials of other calcium phosphate [1-2]. In recent year, DCPD crystal is researched as an environmental treatment material for removing fluoride ions and heavy metal ions from waste water and soil by transition to FAp (fluoroapatite,  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ ) and partly heavy metal substituted-FAp [3].

On the other hands, controlling the shape of such the functional materials attracts material scientist due to increasing their potential as following reasons; their size and surface condition (specific surface area and ratio of the crystal face with good reactivity) rule chemical reactivity and/or responsibility and physical properties. Additionally, after the reaction with target ions, size and shape of sludge sometimes changes their usability. In previous works, plate shaped crystals show good reactivity with fluoride ions; nano-sized precursor often appears at 020 crystal surface. Under aqueous solution synthesis without impurity, DCPD crystals often form plate structure with large 020 crystal surface. But this shaped crystals easily stack each other and without good dynamical property such as mobility and diffusibility. Especially, after the waste water treatment, shape of FAp would change the transit cost of sludge due to its moisture content. Therefore DCPD morphology changing into spherical shaped and located with 020 crystal surface is required.

In past report, we tried to controlling the morphology of DCPD crystals by adding other ions during aqueous synthesis [4], setting the initial pH value and concentrations of calcium ion and phosphate ion [5]. And we succeeded to change the morphology of DCPD crystals from plate-like structure to petal-like structure by preceding parameters. But the results shows paradoxical with usual crystal growth; under crystal growth condition with higher concentration, morphology of DCPD crystals becomes to single crystal-like plate structure and under lower concentration, morphology changes to multi-crystals; aggregation of plate structure (petal). In typical crystallography, under higher concentration condition, many crystal nuclei appear everywhere and they aggregate with each other. Therefore, morphology changing of DCPD crystals shows unique phenomenon.

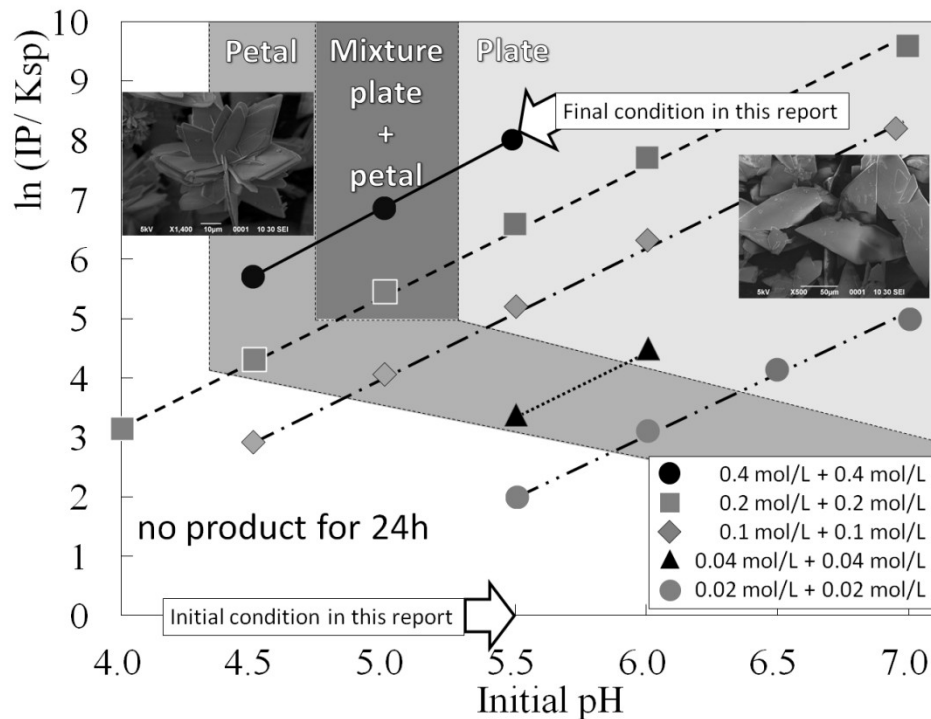
Here we report to unveil the mechanism of morphology changing of DCPD crystals by very simple approach; by changing the mixing process of two solutions. We designed the synthesis process; initial crystallization condition was set under the condition with petal-like structure and crystal growth condition was set under the condition with plate-like structure. Solid phase products were observed by scanning electron microscope (SEM). Mixing process designing changed the morphology of final products.

## 2. Experimental Method

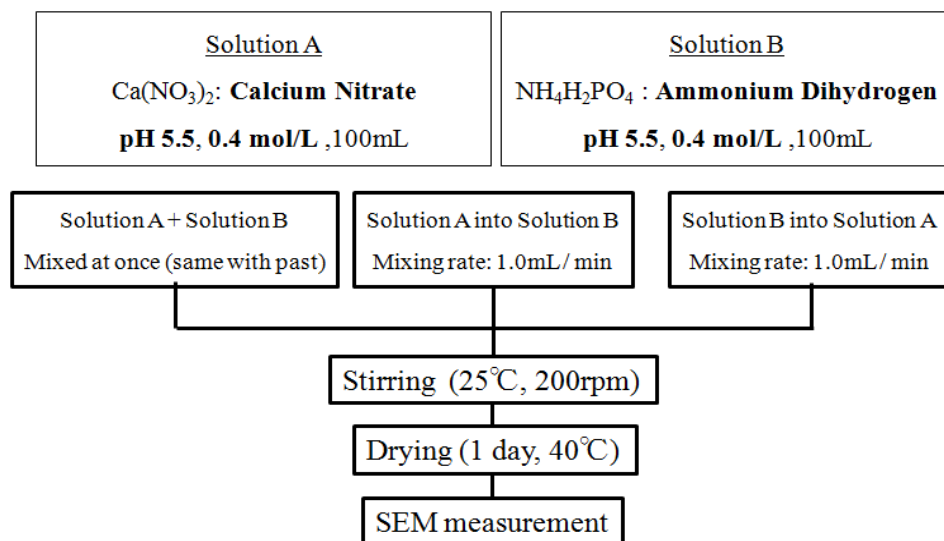
### 2.1. Strategy for Unveiling mechanism of Morphology changing

In crystallography, morphology changing mechanisms is classified two types; one is depended on the shape of crystal nuclei; crystallization condition rules the morphology and shape of crystal nuclei is kept during crystal growing. And the other one is depended on crystal growing condition; morphology of crystals changed due to anisotropic crystal growth by the difference of crystal growth speed like the Berg effect [6] or difference of stability of crystal face [7].

Therefore, we designed synthesis and judge which mechanisms change the morphology of DCPD crystals. Figure 1 is phase diagram of morphology of DCPD crystal depended on initial pH value and concentration; which is modified from the past report [5]. We started the synthesis at the condition of “no product” and passed the area of “petal-like product”, finally, reached to the condition of “plate-like product”. And we kept the total-environment of crystal growth with same value with last condition. If morphology of DCPD crystals is ruled by initial condition, shape of final products change to petal-like structure, and it is ruled by the environment of crystal growing, shape of final products must be same results with past report [5].



**Figure 1.** Phase diagram of morphology of DCPD crystal depends on initial pH value and super-saturation ratio [5]. Arrowed condition (pH=5.5 and  $\ln(IP/K_{sp})=0$ ) is starting condition and other arrowed condition (pH=5.5 and  $\ln(IP/K_{sp})\approx 8$ ) is final condition of this report.

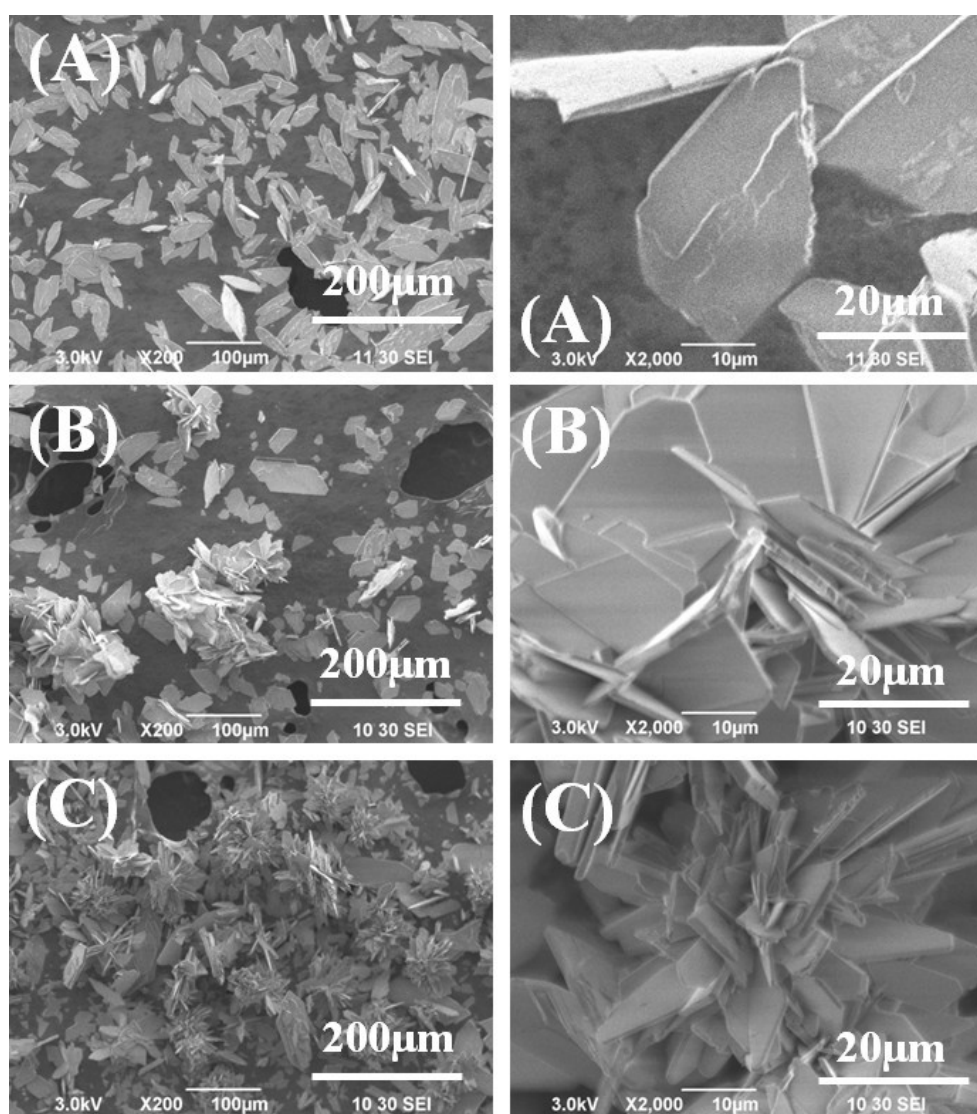


**Figure 2.** Experimental flow diagram of this report. We synthesized DCPD crystals with three-kind processes.

## 2.2. Experimental flowchart

DCPD crystals were synthesized according to the flow diagram shown in Figure 2 under aqueous condition by mixing two solutions; solution A (calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ , Wako, 98.5%)) and solution B (ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ , Nacalai, 99%)), were prepared by dissolving preceding chemicals and adjusted initial concentration and initial pH value by the addition

of 0.01 and 0.1 M nitric acid (Kanto Chemical) and ammonia solution (Wako, 25%). In this report, we set the initial pH value is 5.5 and initial concentration is 0.4 mol/L; in past report, under this condition, all of products form only plate-like structure. Solution A (100 mL) and solution B (100 mL) is mixed (1) at once with stirring (200 rpm) and kept 60 min, this is same process with past report; (2) solution A is dropped into solution B with stirring, the mixing ratio is 1.0 mL /min and stirring speed is same with (1), finish the dropping, we kept stirring 60 min and (3) solution B is dropped into solution A with same process with (2). Obtained solid-products were filtered through a 0.45  $\mu\text{m}$  membrane filter. The solid products were dried at 40  $^{\circ}\text{C}$  for 24 h. The products from each process were observed by SEM (JSM-6390AX, JEOL, accelerating voltage of 3 kV without coating).



**Figure 3.** SEM images of each mixing process. (A) Mixed two solutions at once. (B) Calcium ion solution into phosphate ion solution. (C) Phosphate ion solution into calcium ion solution.

### 3. Experimental Results and Discussions

Figure 3 (A), (B) and (C) are SEM images of products obtained under different mixing processes with magnification 200 and 2000. 3-(A) is the result with process-(1); two solutions were mixed at once and all product form simple plate-like structure, they are same with past report [5]. On the other hands, 3-(B) and 3-(C) are results with process-(2) and (3), respectively. In the case of process-(2),

morphology of products is basically formed with plate-like structure, but few petal-like structured products are also obtained. And in the case of process-(3), most products form petal-like structure and few plate-like structured products are obtained. Our results show the morphology of DCPD crystal is changed only mixing process; this is equal to say, DCPD morphology changing is depended on former mechanism. Incipient crystallization condition changes the shapes of crystal nuclei and they are kept during crystal growing process. At the beginning, crystallization condition is on the area of “no product for 24h” in figure 1. About 5 minutes later from the starting the dropping, crystallization condition would be into the area of “petal-like structure”. And after 7 minute from the starting, concentration of ion would finish the crossing area of “petal-like structure” and be into the area of “plate-like structure”. These times are estimated on simple assumption; each ion would not combine and form DCPD crystals. Actually, staying time on the area of “petal-like structure” would be longer due to DCPD crystallization (But final crystal growth condition is same with (1)). Moreover, shape of one leaf of petal is basically same with plate-like products. Crystal surface is 020 and anisotropic crystal growth direction is same with all mixing process. Therefore, during crystal growing process, shape of product does not change. We also compare the lower initial concentration (0.2 mol/L and the other experimental flow is same), the rate of petal-like structure reduces but same tendency is also obtained.

#### 4. Summary

We synthesized DCPD crystals under aqueous condition and arranged the mixing process of two starting solutions and obtained following results.

(1) Morphology of DCPD crystals is changed from plate structure to mixture condition (plate and petal structure) by changing the mixing process.

We compare the shape of products on mixing process dependency (each starting solutions are set that initial pH value is 5.5 and initial concentration is 0.4 mol/L or 0.2 mol/L) (a) at once and (b) one solution into the other with dropping rate 1.0 ml/min.

(2) Morphology of DCPD crystals is kept during crystal growing and ruled crystal nucleation condition.

Our results suggest that morphology of DCPD crystals is controllable by only setting incipient crystallization condition (and then growth larger with keeping crystal nuclei shape). In future work, we would like to evaluate chemical and physical properties of these petal DCPD crystals.

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#### References

- [1] Kumar M, Dasarathy H and Riley C, 1999 *J. Biomed. Mater. Res.* **45**, 302
- [2] Furutaka K, Monma H, Okura T and Takahashi S. 2006 *J. Eur. Ceram. Soc.* **26**, 543
- [3] Tafu M and Chohji T 2006 *J. Eur. Ceram. Soc.* **26**, 767
- [4] Hamai R, Toshima T, Tafu M, Masutani T, Chohji T, 2013 *Key Engineering Materials*, **529-530**, 55
- [5] Toshima T, Hamai R, Tafu M, Takemura Y, Fujita S, Chohji T, Tanda S, Li S, Qin G W, 2014 *J. Asian Ceramic Soc.* **2**, 52
- [6] Berg W F, 1938 *Proc. R. Soc. London.* **A164** 79
- [7] Kuroda T, Irisawa T, Ookawa A 1977 *J. Cryst. Growth.* **42** 41