

# STRUCTURE CONTROL IN HYDROXYAPATITE SYNTHESIS BY HYDROTHERMAL REACTION AND ORGANIC MODULATORS

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**Abstract** Properties of materials are determined not only by their composition, but also by their structure. It is, therefore, of great significance to develop the ability of tailoring the structure of materials according to the requirements of intended applications. In this work a novel glutamic acid-assisted hydrothermal process was developed to synthesize apatite crystals with controllable morphologies. Varied morphologies from whisk broom, fibers, mushroom, prickly spheres, to dandelion were produced through modulating both the formation of a transitory phase and its transformation into the final phase.

**Keywords** structure control, hydrothermal reaction, apatite

## 1. Introduction

Properties of materials in macro-scale are strongly dependent on the structure at the micro- and nano-scale (Burda et al., 2005). Many remarkable materials created by nature, like bone, cartilage, shells, etc., self-organize to form hierarchical structures, where inorganic crystals co-exist with organic molecules (Stupp & Braun, 1997). Previous investigations reported that fluorine-containing hydroxyapatite of mammalian teeth has ribbon-like morphologies in the initial stage of enamel and develops finally into needle-like crystals, while the apatite crystals in bones are plate-like (Dorozhkin & Epple, 2002). These remarkable structures endow the common material of hydroxyapatite with superior mechanical properties. To obtain such properties, the structure of synthesized hydroxyapatite should be controlled according to specific applications. Although there are many reports on structure control for the synthesis of hydroxyapatite via coprecipitation, sol-gel, solid state reaction, hydrolysis, etc., such structure control capability in these processes is rather limited and the structure that could be synthesized can not be compared with those of materials existing in nature (Weiner & Addadi, 1997).

Inspired by nature, a novel concept of microstructure manipulation with biological organic molecules was proposed several years ago and has been further developed recently (Mann, 2000). Various organic agents have been used to modulate the morphologies of apatite crystals. By means of selective adsorption of surfactants on specific crystal surfaces, the shape control of oxide ceramic nanoparticles has been reported (Zhang & Zhu, 2005). However, changes of interfacial energy alone and hindering effects due to adsorption are not versatile enough to fine-tune the structure of inorganic materials, and can neither produce well-crystallized powders when organic molecules are used in excess. Therefore, more controllable processing parameters are needed to enhance the

structure controllability of inorganic materials.

Here, we propose a novel route in which inorganic materials are synthesized under hydrothermal conditions with the addition of organic molecules as a modulator, by which controllable syntheses unobtainable under normal conditions can be realized by modulating the thermodynamics and kinetics of the overall process. In this work, we take the syntheses of morphologically varied apatites as an example to show our route.

## 2. Experimental

All chemicals were purchased from Beijing Chemicals Corp. and were used as received without further purification. A typical procedure is as follows: appropriate amounts of analytical grade glutamic acid, calcium nitrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), and di-potassium hydrogen phosphate ( $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ ) were dissolved into 100 mL deionized water to form a solution. The solution was then heated to  $\sim 60^\circ\text{C}$  under vigorous stirring, followed by adding appropriate amount of sodium fluoride and potassium hydroxide as the mineralization agents. The as-obtained solution was immediately sealed into an autoclave and hydrothermally treated for 48 hours at different temperatures. After cooling to room temperature, the precipitates were collected and washed several times with deionized water and then with absolute ethanol.

The sizes and morphologies of the as-synthesized powders were characterized by a field emission scanning electron microscope (FESEM, JSM-6700F, JEOL, Japan). Solid phases were identified using an X-ray diffractometer (XRD, X'Pert, PANalytic, The Netherlands) with Cu K $\alpha$  radiation (40 kV, 30 mA).

## 3. Results and Discussion

Figure 1 shows the FESEM images of apatite powders obtained under varied experimental conditions. In the

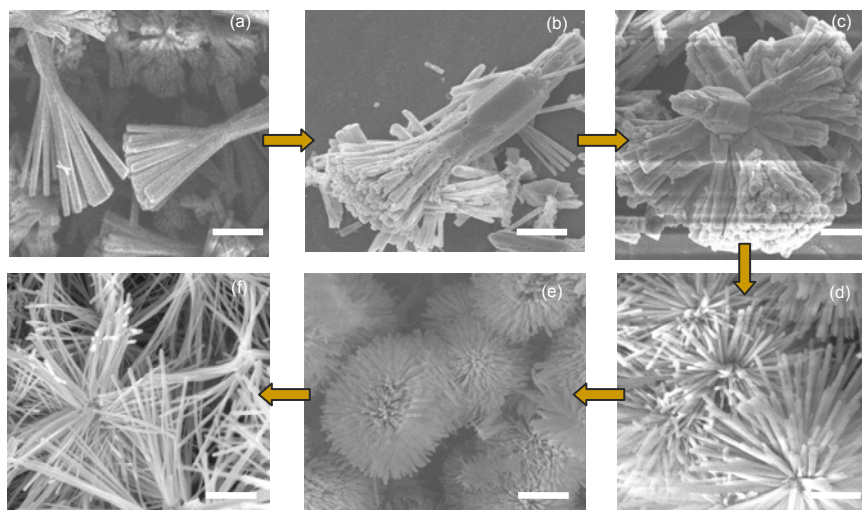


Fig. 1 FESEM images of powders synthesized under different conditions. The experimental conditions:  $C_G/C_{Ca}/C_P/C_F/C_{OH}/T$  = (a) 3.6/1.5/1.21/0.05/0.03/110°C; (b) 3.6/1.5/1.21/0.05/0.03/130°C; (c) 3.6/1.5/1.21/0.07/0.03/130°C; (d) 3.6/1.5/1.21/0.07/0.03/150°C; (e) 3.6/1.42/1.21/0.03/0.8/150°C; (f) 3.6/1.42/1.21/0.03/0.8/160°C. The scale bar is 1  $\mu\text{m}$ .

figure  $C_G$ ,  $C_{Ca}$ ,  $C_P$ ,  $C_F$ , and  $C_{OH}$  indicate respectively the amounts (ingram) of glutamic acid, calcium nitrate, dipotassium hydrogen phosphate, sodium fluoride, and potassium hydroxide in 100 mL deionized water. Temperature is labeled as T in °C.

Under the processing conditions of Fig. 1(a), crystals with whisk broom-like morphology were formed. The formation of whiskers at the end of broom handles could be considered as the results of splitting handle-like crystals. With increasing temperature, as shown in Fig. 1(b), the handle of broom became prismatic with increased diameter. Compared to Fig. 1(a), the number of splitting at the end of broom handles increased significantly while the shape of whiskers of the broom was less uniform. When fluoride concentration was raised in comparison to the condition for Fig. 1(b), mushroom-like morphology was formed in Fig. 1(c). Comprehensive comparison with the morphologies of Figs. 1(a) and (b), showed that the mushroom-like morphology had resulted from the intersection of several whisk broom-like crystals at the end of the handles. Since the morphological development occurred sequentially in time scale, one can infer that it was secondary splitting that formed the mushroom. Primary splitting led to the formation of broom handles, and secondary splitting led to whiskers radiating out the ends of the handles.

For experiment at 150°C and higher, one of the above-mentioned two splitting mechanisms disappeared. As a result, long needle-like crystals rayed out from their centers to form a dandelion-like morphology, see Fig. 1(d). The diameter of needle-like crystals was about 100 nm while the overall size of dandelion was about 3  $\mu\text{m}$ . When more KOH than NaF was used as the mineralizing agent, much more needle-like crystals appeared than in Fig. 1(d), as shown in Fig. 1(e), radiating from the centers to form fully-developed prickly spheres with overall size of ~3  $\mu\text{m}$ .

When the temperature was raised to 160°C, the prickly spheres opened with ultralong fibers. Although the fibers were tangled together, it is clear that they all radiated from their respective centers as shown in Fig. 1(f). The diameters of the fibers centers were all less than 100 nm though their lengths were more than several micrometers. Fibers with such high aspect ratio may be used to reinforce polymer or calcium phosphate ceramics.

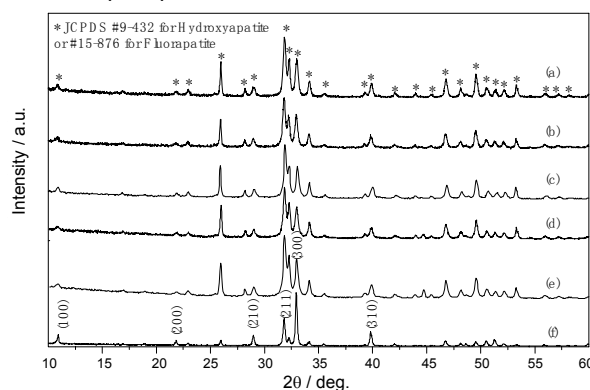


Fig. 2 XRD patterns of apatite powders synthesized under different conditions. The experimental conditions:  $C_G/C_{Ca}/C_P/C_F/C_{OH}/T$  = (a) 3.6/1.5/1.21/0.05/0.03/110°C; (b) 3.6/1.5/1.21/0.05/0.03/130°C; (c) 3.6/1.5/1.21/0.07/0.03/130°C; (d) 3.6/1.5/1.21/0.07/0.03/150°C; (e) 3.6/1.42/1.21/0.03/0.8/150°C; (f) 3.6/1.42/1.21/0.03/0.8/160°C.

Figure 2 shows the XRD patterns of the powders synthesized under different conditions, which correspond to the images in Fig. 1. All these patterns confirmed that the as-synthesized powders were of apatite structure without any impure phases. Splitting into four peaks around 30°–35° indicates that the powders synthesized were well-crystallized apatite. The variation of relative peak intensities could be attributed to the special morphologies and the preferred orientations during preparation of the

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