Morphology variation of cadmium hydroxyapatite synthesized by high
temperature mixing method under hydrothermal conditions

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Abstract

Cadmium hydroxyapatite (Cd HAp) pure crystals were synthesized by high temperature mixing method under hydrothermal conditions using the solutions of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$. The influences of pH values and reaction time on the structure and morphology of Cd HAp crystals were investigated. The results indicate that the pH value has a great influence on the morphology which varies from bulk-like to fiber with the increase of the pH value. The intermediate phase of $\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ is formed in the weak alkali reaction medium of $(\text{NH}_4)_2\text{HPO}_4$ at $\text{pH} = 9$, and it takes long time to be dissolved and changed into pure phase of bulk-like Cd HAp crystal. In the strong alkali reaction medium of $(\text{NH}_4)_2\text{HPO}_4$ solution at $\text{pH} = 11$, the intermediate phase of $\text{Cd}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ is formed, and then dissolved, and rapidly changed to pure phase of Cd HAp fiber. $\text{Cd}_3(\text{OH})_5\text{NO}_3$ crystals are formed in the nitrate solution before mixing at 200°C , its influences on crystallinity, morphology and size of Cd-HAp crystals were also discussed.

Keywords: Cadmium hydroxyapatite; Morphology; Hydrothermal method; High temperature mixing method

1 Introduction

Calcium Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; Ca-HAp) with a typical apatite structure shows a high capacity for substitution of Ca ions by heavy metal ions due to its crystal structure and chemical composition, and it has been used to remove toxic heavy metal ions from industrial waste water [1]. It is also the major constituent of the skeleton and teeth of vertebrates [2].

As a part of studies on the apatite group compounds, Cd HAp pure phase was synthesized by many investigators using hydrolysis and hydrothermal reactions [3–9]. The previous studies, however, showed only powder X-ray diffraction (XRD) patterns [3-6], unit-cell dimensions [7,8], thermal behavior [5,6] and IR spectra [7] of Cd HAp and few reports have been presented on the investigation of a relationship between synthetic conditions and properties of the formed particles, such as crystal phase, composition, morphology and crystallinity. Yasukawa et al. [10] have prepared needle-like cadmium hydroxyapatite particles by a two-steps wet method with acetamide, and reported the relationship between the shape of the particle and synthesis conditions.

Hydrothermal method is a wet-chemical technique for directly forming complex oxide powders with high crystallinity [11]. The technique has an additional advantage

for the preparation of HAp powders: no hydroxyl defects in the structure. Cd HAp [12], Ca-Cd HAp [13, 14], Ca-Sr HAp [14, 15] and Sr-Pb HAp [16] were successfully synthesized hydrothermally in our former works. On the base of hydrothermal method, a new technique (high-temperature mixing method, HTMM) for preparation of powders in multi-component system such as hydroxyapatite under hydrothermal conditions was designed [17]. In this technique, two kinds of starting solutions separately heated to a desired reaction temperature in a multi-chamber autoclave were mixed to start the reaction under hydrothermal conditions. Ca-Cd HAp [13] and Ca-Sr HAp [15] were successfully synthesized by HTMM in our former works.

The objective of this work is to study the effects of reaction conditions such as pH value, reaction temperature and time on the crystalline phase, composition and particle morphology of the products in the system of Cd^{2+} - PO_4^{3-} - H_2O system synthesized by HTMM under hydrothermal conditions.

2 Experimental Procedures

2.1. Preparation

The starting materials are 0.334 mol/dm³ cadmium nitrate tetra hydrate (Cd(NO₃)₂·4H₂O, 99.0%, Wako Pure Chemical, Japan) and 0.200 mol/dm³ diammonium hydrogen phosphate ((NH₄)₂HPO₄, 99.0%, Wako Pure Chemical, Japan) solutions. The pH value of the phosphate solution was adjusted to 6-11 by ammonia.

The hydrothermal reactions were carried out in a Teflon lined multi-chamber autoclave [17] with inner volume of 50 cm³, which has two chambers with inner volume of 12.5 cm³ each in the autoclave. The starting solutions (8 cm³ each) were separately placed in each chamber to get the stoichiometric composition of Cd HAp. After sealing, the autoclave was putted into the oven. Then, the oven was heated to a desired temperature with a heating rate of (180°C/h). The autoclave was connected to the rotation shaft in the oven, and the rotation was started to mix the starting solutions at a desired temperature. Thus, the freshly formed precipitate was hydrothermally treated with agitation. Hydrothermal treatments were mainly conducted at 200°C for 12 hours.

2.2. Characterization

After the hydrothermal treatments, pH of the solutions was measured and the solid products were collected by centrifuge after washing with water. The products were

characterized by powder X-ray diffraction (XRD; Model RTP-300RC, Rigaku Co., Japan) with Cu K α radiation (40kV and 100 mA), scanning electron microscopy (SEM; Model S530, HITACHI Co., Japan). The concentration of Cd and P in the solutions after the hydrothermal treatments was measured by inductively coupled plasma (ICP) spectrometry (SPS7000A, Seiko).

3. Results

3.1 Effect of pH value in the reaction medium.

It is reported in our former work [12] that the pH values of the solutions after reaction are below 2 when the pH values of the (NH₄)₂HPO₄ solutions are less than 9. On the other hand, the pH values of the solutions after reaction are over 8 when the pH values of the (NH₄)₂HPO₄ solutions are more than 10.

The XRD patterns of the products prepared by HTMM from (NH₄)₂HPO₄ solutions with different pH values are shown in Fig. 1. Cd₅H₂(PO₄)₄·4H₂O is formed from the acidic (NH₄)₂HPO₄ solution at pH = 6. When the pH values of (NH₄)₂HPO₄ solutions are over 7, Cd HAp is formed as a single phase. However, a small difference in the

intensity of the diffraction peaks was observed. The intensity of (300) diffraction increase in comparison with that of (114) diffraction, when the pH value of phosphate solutions is 10. The results suggest that Cd HAp crystals obtained in phosphate solutions with low pH are plate-like in (001) and with those obtained at high pH are acicular in the c direction. However, the peaks become broader when the pH value of phosphate solutions is 11. The extra experiments were done to clarify it. It is found that $\text{Cd}_3(\text{OH})_5\text{NO}_3$ crystals are formed in the nitrate solution before mixing at 200°C (see Fig. 2). The unknown crystal coexists with $\text{Cd}_3(\text{OH})_5\text{NO}_3$ crystals when the pH value of phosphate solutions is 11. The amount of this compound increase with the increase in the Cd content of the solution (see Fig. 3). The precipitation of $\text{Cd}_3(\text{OH})_5\text{NO}_3$ must result in the decrease of the Cd content in the nitrate solution. When two solutions are mixed at 200°C, the $\text{Cd}_3(\text{OH})_5\text{NO}_3$ should be dissolved firstly. Thus, the aggregated crystals are obtained. The hydrothermal treatment might increase the compositional homogeneity of the products by dissolution and precipitation mechanism. However, some compositional inhomogeneity remains in the products, which might give the broad X-ray diffraction patterns.

Fig. 4 shows SEM photographs of the products prepared by HTMM from $(\text{NH}_4)_2\text{HPO}_4$ solutions with different pH values. The aggregated bulky crystals of

$\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ are formed from the phosphate solution with pH of 6. When the pH value of phosphate solutions is in the range of 7 to 9, the Cd HAp crystals are all stubby hexagonal prismatic and the size of the crystals decrease with the increase of pH value. When the pH value of phosphate solutions is 10, the Cd HAp crystals change from stubby hexagonal prismatic to needle-like in shape. And when the pH value of phosphate solutions is 11, the Cd HAp crystals change from needle-like in shape to fiber. Thus, the difference in the XRD intensity can be explained by the morphological change of the Cd HAp crystals.

3.2 Influence of reaction time on the formation of Cd HAp in the reaction medium with different pH value.

In order to investigate the growth process, hydrothermal treatments were conducted using phosphate solutions with different pH values of 9 (the reaction medium is acid solution with pH value of about 2) and 11 (the reaction medium is alkaline solution with pH value of about 9.6) by changing reaction time. The reaction time of 0 h means that the autoclave is quenched directly after the temperature reached 200°C.

The XRD patterns and SEM photographs of the products obtained from phosphate

solution with pH of 9 by varying reaction time are shown in Fig. 5 and 6, respectively. Cadmium phosphate hydrate ($\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$) coexists with Cd HAp crystals at 200°C for 0h. After 1/3 h, the pure phase of Cd HAp is obtained. The crystals obtained by quenching to room temperature just after the temperature reached 200°C, are aggregated large rods in shape of $\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ and small rods in shape of Cd HAp (Fig. 6-a). After 1/3 h, the bulky shaped Cd HAp crystals are formed by the hydrothermal reaction, and the crystals grow slowly with the increase of the reaction time.

The XRD patterns and SEM photographs of the products obtained by HTMM from phosphate solution with pH of 11 varying reaction time are shown in Fig. 7 and 8, respectively. After mixing at 200°C, the $\text{Cd}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ crystals are formed and rapidly changed to Cd HAp by quenching to room temperature, the crystals of $\text{Cd}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ are plate-like in shape and highly aggregated, which coexist with the aggregated small rod crystals of Cd HAp with low crystallinity (Fig. 8-a). After 1/3 h of reaction time at 200°C, the rod-like crystallite of Cd HAp with low crystallinity is formed, and changed to needle after 5 h, and then changed to fiber after 12 h.

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4. Discussion

In this work, shape of the Cd HAp crystals clearly change from bulky in the range of pH 7–9 to rod and fiber in the range of pH 10–11 of the phosphate solutions. But It is found that Cd HAp is not formed directly, but form through the intermediate phases. The $\text{Cd}_3(\text{OH})_5\text{NO}_3$ crystals are formed in the nitrate solution before mixing at 200°C (see Fig. 2), and then changed to $\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ at low pH and $\text{Cd}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ at high pH. The detailed formation mechanism of Cd HAp is similar to that in our former work [12]. In this work, the $\text{Cd}_3(\text{OH})_5\text{NO}_3$ crystals resulted in the decrease of the Cd HAp crystallinity and the formation of fibre. In addition, the formation mechanism of Cd HAp is a little different from our former work [12]. When the pH value of the starting phosphate solution is 9, the Cd HAp crystals was formed after 1/3 hours and changed to rod-like, but it was formed after 5 hours and changed to stubby hexagonal prismatic in our former work [12]. When the pH value of the starting phosphate solution is 11, the Cd HAp crystals was formed after 1/3 hours and changed to fibre, but it was formed after same time and changed to rod-like in our former work [12].

The size of the Cd HAp crystals obtained though $\text{Cd}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ by using $(\text{NH}_4)_2\text{HPO}_4$ solution with pH 10 is smaller than that with pH 11, and it also grow largely with the increase of reaction time. The size change of Cd HAp crystals may be

explained by the solubility of Cd HAp in a solution with different pH value. If the solubility of Cd HAp in a solution is low, Cd HAp crystals cannot grow larger by the Ostwald ripening. The concentrations of the solutions after hydrothermal treatment might give some information on the solubility of the solid products. Concentrations values for Cd^{2+} and PO_4^{3-} are given in Table 1. The $(\text{NH}_4)_2\text{HPO}_4$ solution with pH 10 gives the lowest concentrations of both Cd^{2+} and PO_4^{3-} . It is expected from the estimated solubility that the size of the Cd HAp crystals increases with the increase in pH value from 10 to 11.

In addition, the size of Cd HAp crystals synthesized by HTMM in this work is smaller than that synthesized by LTMM in our former work. It can be explained that $\text{Cd}_3(\text{OH})_5\text{NO}_3$ crystals are formed in the nitrate solution before mixing by heating to 200°C , and then dissolved to form intermediate phases, $\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ at low pH and $\text{Cd}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ at high pH. Therefore, the smaller Cd HAp crystals with stubby hexagonal prismatic in shape are formed in the reaction media with low pH, and the Cd HAp fibers are formed in the reaction media with high pH of 11.

5. Conclusions

The Cd HAp crystals with high crystallinity were synthesized by HTMM under

hydrothermal conditions at 200°C for 12 hours when the pH values of the starting $(\text{NH}_4)_2\text{HPO}_4$ solution solutions are over 7. In the acid phosphate solution with pH value 6, $\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ is formed instead of Cd HAp. The morphology of Cd HAp crystals varies from stubby hexagonal prismatic to needle and fiber with the increase in pH. The intermediate phase of $\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ is formed in the acid reaction media, and changed into Cd HAp rapidly. In the alkaline reaction media, the intermediate phase of $\text{Cd}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ is formed, and rapidly changed to the Cd HAp, which give smaller bulky, needle and fiber Cd HAp crystals. $\text{Cd}_3(\text{OH})_5\text{NO}_3$ crystals are formed in the nitrate solution before mixing at 200°C, which results in the formation of smaller Cd HAp crystals in size compared to the results of Cd HAp synthesized by LTMM.

Acknowledgements

The authors would like to thank the financial support from Jiangsu provincial natural science foundation of China (BK2007200) and the Fostering Fund of the Ministry of Education (No. 707031).The authors acknowledge fruitful discussions with Dr. Bao Ningzhong.

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Picture captions

Fig. 1. X-ray diffraction patterns of the products prepared by HTMM at 200°C for 12 hours from the $(\text{NH}_4)_2\text{HPO}_4$ solution with different pH value: (a) 6, (b) 7, (c) 8, (d) 9, (e) 10, (f) 11. ●: $\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$

Fig. 2. X-ray diffraction patterns of $\text{Cd}_3(\text{OH})_5\text{NO}_3$ formed in the $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution before mixing with $(\text{NH}_4)_2\text{HPO}_4$ solution with different pH values at 200°C.

Fig. 3. The weights of $\text{Cd}_3(\text{OH})_5\text{NO}_3$ powders formed in the $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution before mixing with $(\text{NH}_4)_2\text{HPO}_4$ solution with different pH values at 200°C.

Fig. 4. SEM micrographs of the samples prepared by HTMM at 200°C for 12 hours using the starting solutions of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ with different pH values: (a) 6; (b) 7; (c) 8; (d) 9; (e) 10; (f) 11.

Fig. 5. X-ray diffraction patterns of the products obtained by HTMM from $(\text{NH}_4)_2\text{HPO}_4$ solution with pH 9 at different conditions, (a) 200°C, 0 h, (b) 200°C, 1/3 h, (c) 200°C, 5 h and (d) 200°C, 12 h. ♦: $\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$

Fig. 6. SEM micrographs of the samples prepared by HTMM using the starting solutions of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ with pH value 9 at 200°C for different time: (a) 0h (b) 20 minutes (c) 5h and (d) 12h.

Fig. 7. X-ray diffraction patterns of the products obtained by HTMM from $(\text{NH}_4)_2\text{HPO}_4$ solution with pH 11 at different conditions, (a) 200°C, 0 h, (b) 200°C, 1/3 h, (c) 200°C, 5 h and (d) 200°C, 12 h. ∇: Cd HAp ♦: $\text{Cd}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$

Fig. 8. SEM micrographs of the samples prepared by HTMM using the starting solutions of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ with pH value 11 at 200°C for different time: (a) 0h (b) 1/3h (c) 5h and (d) 12h.

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