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The influence of pH and temperature on the morphology of hydroxyapatite synthesized by hydrothermal method

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Abstract

Hydroxyapatite (HA) whiskers and crystals were synthesized by hydrothermal treatment of $Ca(OH)_2$ and $CaHPO_4{\cdot}2H_2O$. Different conditions relative to pH = 6–14, temperature = 60–140 °C have been investigated in order to ascertain their influence on the HA particle structure and morphology. Results have shown that pH value is a significant parameter variable in altering the morphology. Well elongated particles were obtained on condition that pH = 9 and temperature = 120 °C. These HA whiskers were single crystals with an aspect ratio > 20, a typical diameter and length of 40 and 600 nm, respectively.

Keywords: Hydroxyapatite; Hydrothermal

1. Introduction

Hydroxyapatite (HA), with compositions of stoichiometric $Ca_{10}(PO_4)_6(OH)_2$ and Ca/P = 1.67 [1], has been studied for many years, due to its similarity with the mineral constituents of human bones and teeth [2]. For load-bearing orthopedic and dental applications, densified HA powders are widely needed. However, dense HA ceramics have always showed a lower tensile strength compared with the values of human bones [3]. Whiskers have generally exhibited high tensile properties because of their low dislocation density [4]. With this view, whisker-like or needle-like crystals of HA have been synthesized in recent years for improving the fracture toughness.

HA can be synthesized by a variety of methods such as solid-state reaction [5], co-precipitation [6], sol-gel [7,8], sputtering [9]. In spite of the large amount of preparation procedures, only a few have been devoted to synthesizing apatitic compounds with morphology controlled. In contrast, hydrothermal methods using elevated temperature and pressure aqueous solutions [10] allow the synthesis of HA crystals with a certain shape. Although the needle-shaped HA ceramics have been prepared by hydrothermal method, the procedure was relatively complicated or the treating temperature was comparatively high. In this paper, fine HA single crystals of high crystallinity with homogeneous rod shapes have been synthesized by a simple method at comparatively low temperature. $Ca(OH)_2$ and $CaHPO_4{\cdot}2H_2O$ have been utilized as starting materials, no additives such as K_3PO_4 or EDTA were necessary. Hydrothermal processing results in pure HA powders as product obtained finally and corresponding hydrothermal reaction occurs as follows:

$$4Ca(OH)_2+6CaHPO_4{\cdot}2H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2+18H_2O$$

The influences of pH value and treating temperature have been investigated in our study. It indicates that the different selections of pH value and hydrothermal temperature are critical for obtaining desirable HA morphology.

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2. Experimental

2.1. Procedure

The initial reaction substances of $CaHPO_4{\cdot}2H_2O$ (0.5162 g) and $Ca(OH)_2$ (0.1482 g) were dissolved in 40 ml deionized water.

To investigate the influence of pH value, a series of experiments were devised. First the solutions with different pH were acquired. The pH of initial solution without adjusting was 12. The CH_3COOH solution was used to adjust pH of solution to 6 and 9, respectively. For pH = 14, the initial solution was adjusted by adding KOH solution. The ready-adjusted solutions with certain pH value were put in a teflon vessel and heated at temperature 140 °C for 24 h, and then cooled to room temperature naturally. After that the precipitates were filtered and washed with deionized water till the pH turned to 7. Finally, the filtrates were dried in vacuum at 60–100 °C for 2 h.

2.2. Characterization

X-ray diffraction (Rigaku D/Max-3C, Cu K_α radiation) was utilized to identify the phase produced. Fourier transform infrared absorption spectra (FTIR) were obtained by using a Nicolet Magna-IR 560 spectroscopy. The particle size and morphology were investigated by scanning electron microscopy (SEM, Model S-4500, Hitachi, Tokyo, Japan) and transmission electron microscopy (TEM, Model Hitachi H-700H, 200 KV).

3. Results and discussion

3.1. The initial solution without adjusting pH value

The XRD pattern of powders synthesized by hydrothermal treatment of the solution only containing $CaHPO_4{\cdot}2H_2O$ and $Ca(OH)_2$ at 140 °C for 24 h, is given in Fig. 1. The XRD peaks were attributed not only to HA lattice planes, but also to monetite [11] lattice planes. This phenomenon indicates that monetite phase, which is dominant in the product, coexists with HA. Thus, pure HA phase can't be acquired at 140 °C by this route if the pH value of the initial solution was not adjusted.

3.2. Effect of pH

The XRD patterns of HA powders synthesized with different pH value, which was varied from 6 to 14, are shown in Fig. 2. All these three traces in the XRD patterns showed that pure HA powders had been synthesized via hydrothermal processing with pH of starting reaction solution adjusted to 6, 9 and 14. No peaks

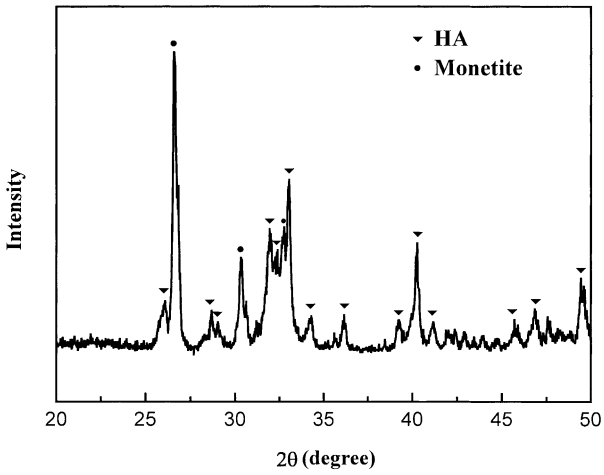


Fig. 1. The XRD pattern of powder samples obtained by the hydrothermal treatment of the initial solution without adjusting pH value.

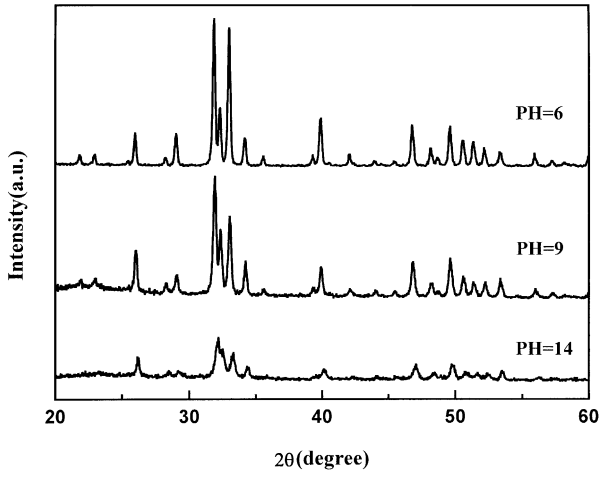


Fig. 2. The XRD patterns of HA powders synthesized with a different pH value.

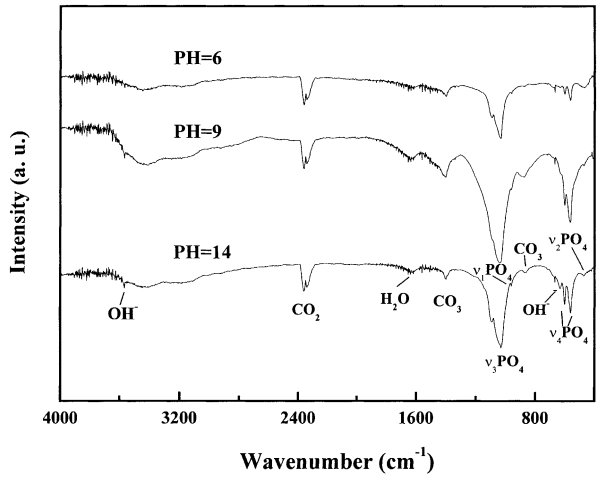
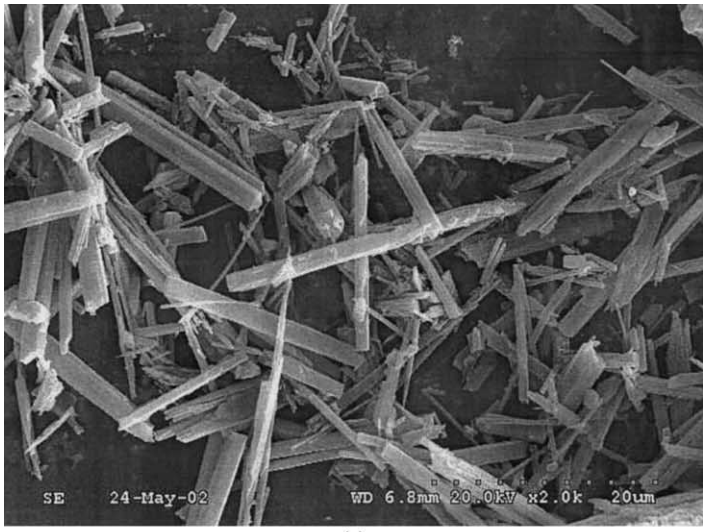
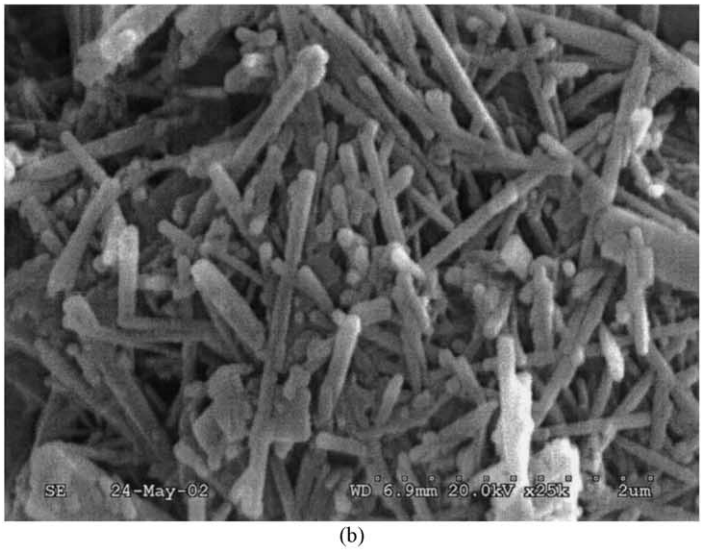


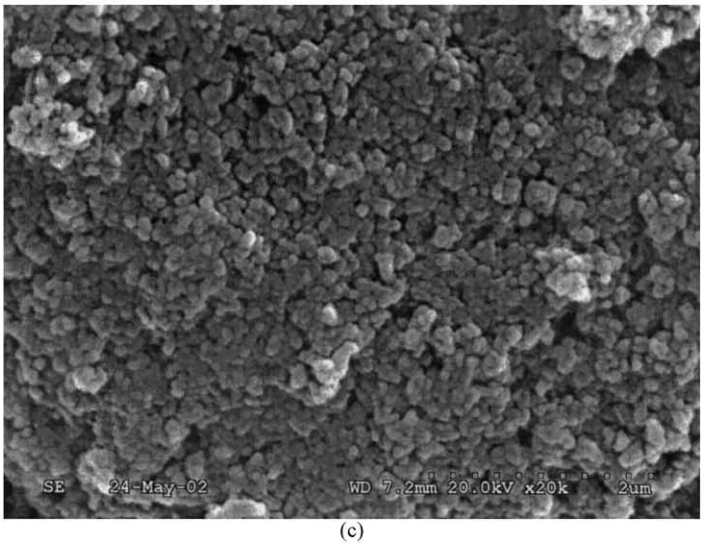
Fig. 3. The FTIR spectrum of HA powders synthesized with a different pH value.



(a)



(b)



(c)

Fig. 4. SEM micrographs of HA whiskers and crystals with a different pH value at the same temperature 140 °C: (a) pH = 6, (b) pH = 9, (c) pH = 14.

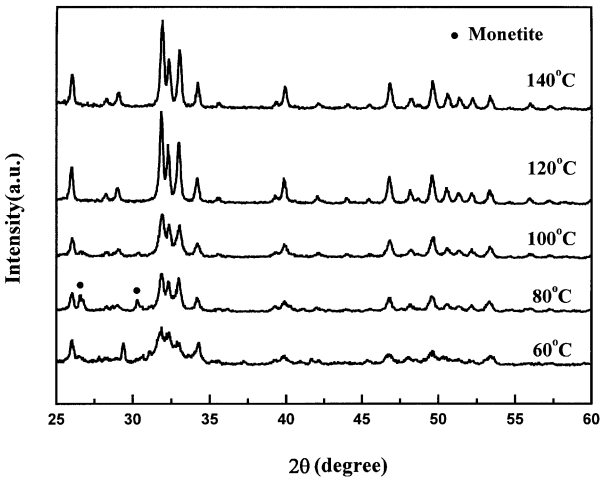


Fig. 5. The XRD patterns of HA powders synthesized at a different temperature with the same pH = 9.

corresponding to monetite or other impurity were found in each trace. Although the traces represented the characteristic XRD pattern for pure hydroxyopatite, the intensities of the 211 and 300 planes were changed because of the whisker orientation. This result was also the case for previous reports [12,13] about hydrothermally-synthesized HA whiskers, which were apparently elongated along the *c* axis. For pH = 6 and 9, many sharp peaks appeared, suggesting that the samples were well crystallized. However, the HA powders obtained from the solution of pH = 14 showed comparatively low crystallinity.

The FTIR spectra of the samples mentioned above are given in Fig. 3. No marked difference has been observed in this figure. This is a typical spectrum for stoichiometric HA, showing PO_4-derived bands at 474, 571, 601, 962, and 1032–1087 cm^{-1} [14]. Some CO_3-derived bands are observed at 870 cm^{-1} and around 1420–1480 cm^{-1}. It might be due to the adsorption of atmospheric carbon dioxide during the sample preparation. This small amount of CO_3 has not produced either CO_3-substituted HA (as evident by XRD) or other carbonates. Low intensity OH-derived bands at 630 and 3570 cm^{-1}, which are typical of stoichiometric HA, are also observed.

Fig. 4 shows the SEM micrographs of hydrothermal-synthesized HA powders obtained from the solution of pH = 6, 9 and 14. Samples synthesized by the solution of pH = 6 and 9 exhibited almost whisker morphologies. For pH = 6, the aspect ratios (i.e. length/diameter) ranged from 3 to 10, with the median whisker diameter and length equal to 2 and 20 μm, respectively. For pH = 9, HA powder samples exhibited the formation of monodisperse, but much thinner, HA whiskers with an aspect ratio > 20 and a typical diameter and length of 100 nm and 2 μm, respectively. On the other hand, from the SEM micrograph of HA powder samples obtained from the solution of pH = 14, morphology distinct from other samples was observed. The average particle size was 150 nm.

Although no apparent difference was seen from XRD patterns of HA powder samples synthesized at different pH of 6 and 9, the pH 14 condition gave a material of poorer crystallinity. Furthermore, the morphology of all the samples above changed obviously. Whiskers with the higher aspect ratio were obtained at relative low temperature with reaction solution of pH = 9. This indicates that pH value is a significant parameter variable in altering the morphology.

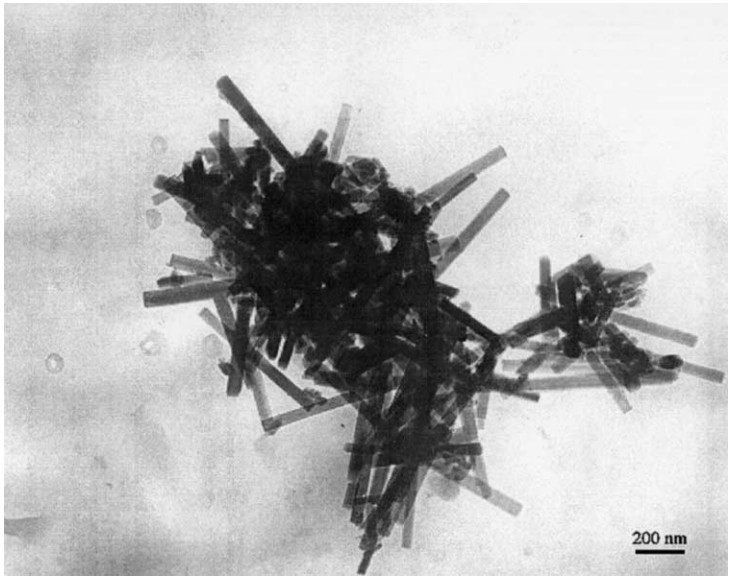


Fig. 6. TEM micrograph of HA powders synthesized at 120 °C for 24 h.

3.3. Influence of temperature

To obtain the HA whiskers at lower feasible temperature, a series of experiments was designed. The pH values of initial solutions were all adjusted to 9 by CH_3COOH solution, and hydrothermal temperature ranged from 60 to 140 °C for 24 h.

Fig. 5 shows the XRD patterns for HA powder samples synthesized at temperature 60, 80, 100, 120 and 140 °C. As seen from the XRD pattern for the sample synthesized at 60 °C, peaks corresponding to HA had begun to appear. At this temperature, the peaks were ill-defined which were indicative of weak scattering from this phase. At 80 °C, the peaks ascribed to monetite, can be seen along with the peaks representing HA. However, with the treatment temperature going up, the peaks corresponding to HA became more and more dominant, and the peaks for monetite decreased. At 120 °C, the peaks attributed to monetite all disappeared and pure HA phase powders were obtained.

Fig. 6 shows the TEM micrograph of HA powders synthesized at 120 °C for 24 h. The needle-like crystals with uniform particle size had been obtained with this condition. The aspect ratios (i.e. length/diameter) ranged from 8–20, with the median whisker diameter and length being 40 nm and 600 nm, respectively. Therefore, it is possible to synthesize homogeneous HA nanowhiskers with high aspect ratio at lower temperature.

4. Conclusions

Fine hydroxyapatite single crystals were synthesized by a hydrothermal method with $Ca(OH)_2$ and $CaHPO_4 2H_2O$ as starting materials. The pH value of the starting reaction solution and the temperature of hydrothermal treatment are the most significant variables in altering the HA structure and morphology. Whiskers with high aspect ratio were obtained from the starting reaction solution of pH = 9 at the relatively low temperature of 120 °C.

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