O U R N A L O F

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# Preparation of carbonated apatite nano-whiskers in SBF with ultrasonic assistance

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Carbonated apatite nano-whiskers were prepared in simulated body fluids (SBF) with ultrasonic assistance at 37 °C. The effects of the initial pH value in the SBF solution and reaction times were investigated in this study. The calcium phosphate precipitates were examined by XRD, FTIR and TEM techniques. The results showed that the initial pH value in the SBF had an important effect on the morphology and composition of the calcium phosphate precipitates, and carbonated apatite nano-whiskers with length/diameter ratio of ~20 were obtained at an initial pH = 7.5 after ultrasonic treatment for 24 h.

Key words: Carbonated apatite, Nano-whisker, Simulated body fluids, Ultrasonic assistance.

## Introduction

Carbonated apatite (denoted as CAP) is the mineral phase of bone and teeth [1-3]. CAP have attracted substantial attentions due to its biocompatibility and bioactivity, the ability to form a chemical bond in the interface between an implant and living tissue. Furthermore, CAP can be used in industrial fields such as for separation and adsorption because of its specific surface structure [3]. CAP is limited to application in the non-loaded or low-loaded fields due to its brittle nature. Recently, CAP has been introduced to fill polymer matrix to improve its mechanical properties [4, 5]. Generally speaking, crystal whiskers are free from the internal defects such as dislocations due to their small diameter and its strength tends to the maximum theoretical value [6]. Hence, various methods have been employed to prepare CAP whiskers, including co-precipitation, homogeneous precipitation, sol-gel synthesis, pyrolysis of aerosols, using a micro-emulsion and hydrothermal reaction. [7-11]

In this study, simulated body fluid (SBF) was used as a medium to prepare CAP nano-whiskers in order to simulate the biological environment in human bodies. Ultrasonic treatment was also used to reduce the aging time.

## Experimental

## Materials and methods

The starting materials were listed as follows:  $K_2HPO_4 \cdot 3H_2O$ , CaCl<sub>2</sub>, sorbitol (C6H14O6), NaCl, NaHCO<sub>3</sub>, KCl, K<sub>2</sub>HPO<sub>4</sub> \cdot 3H<sub>2</sub>O, MgCl<sub>2</sub> · 6H<sub>2</sub>O, 1 mol/l HCl, CaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub> and (CH<sub>2</sub>OH)<sub>3</sub>CNH<sub>2</sub>. A simulated body fluid (SBF) solution

was prepared according to the method developed by Kokubo *et al.*[12]

Firstly, K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O (0.012 mol) and sorbitol (0.04 mol) were dissolved into 100 ml SBF to form a phosphate solution. Secondly, CaCl<sub>2</sub> (0.02 mol) was dissolved into 100 ml SBF to obtain a calcium solution. Then, a milky suspension appeared after adding phosphate solution dropwise into the calcium solution with an initial Ca/P ratio of 1.67 (stoichiometric ratio of HA) at different initial pH values of 7.15 to 7.80. The milky suspension was aged for 1 h under continuous and gentle magnetic stirring, and put into an ultrasonic bath at 37 °C with an ultrasonic power of 40 W. The suspensions were treated ultrasonically for different times of 6-24 h. After the treatment, the calcium phosphate precipitates were filtered and washed twice with deionized water and then with anhydrous ethanol twice, to remove the residual sorbitol and ions. The filtered cakes were dried at 70 °C for 24 h to obtain calcium phosphate powders.

## Characterization

X-ray diffraction (XRD, ARL X'TRA. Cu K $\alpha$  radiation) was employed to characterize the phase of the calcium phosphate precipitates. Fourier transformed infrared spectroscopy (FTIR, Nexus 670. Resolution: 2 cm<sup>-1</sup>) was conducted in the wave number range of 4000-400 cm<sup>-1</sup>. High resolution transmission electron microscopy (TEM, JEM-2010 UHR, accelerating voltage: 200 kV; crystal lattice resolution = 0.143 nm) was used to observe the calcium phosphate precipitates.

## **Results and Discussion**

Fig.1 shows the XRD patterns of the Samples 1#, 2#, 3# and 4# prepared at the initial pHs in the SBF solution of 7.15, 7.30, 7.50 and 7.60, respectively, after ultrasonic treatment for 24 h. It can be seen that when the initial pH was

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**Fig. 1.** XRD patterns of samples 1#, 2#, 3# and 4# prepared at initial pHs in the SBF solution of 7.15, 7.30, 7.50 and 7.60, respectively, after ultrasonic treatment for 24 h.

7.15, The main phase is CaHPO<sub>4</sub> and only a few CAP peaks were observed. When the initial pH was higher, the yield of CAP increased and only the CAP phase could be obtained if pH  $\geq$  7.45. The reaction may be described by Eq.1:

 $CaHPO_4 = Ca^{2+} + HPO_4^{2-}$ (1)

$$HPO_4^{2-} = PO_4^{3-} + H^+$$
(2)

$$10Ca^{2+} + 6PO_4^{3-} + 2H_2O = Ca_{10}(PO_4)_6(OH)_2$$
(3)

$$6CaHPO_4 + 4Ca^{2+} + 2H_2O = Ca_{10}(PO_4)_6(OH)_2 + 8H^+ \quad (4)$$

When the initial pH in the SBF solution was higher, the reaction would be more easily progressed to the right direction for preparing  $Ca_{10}(PO_4)_6(OH)_2$  as described in Eq.4.

Fig.2 gives the XRD patterns of samples 5#, 6#, 7# and 8# prepared at an initial pH = 7.45 in SBF solution after ultrasonic treatment for 6, 12, 18 and 24 h, respectively. The intensity of the (002) peak is much higher than that of standard apatite (JCPDS card No. 9-432). This may be due to the predominant crystal growth along the c-axis, which could make the precipitates to be whiskers. Furthermore, there is no obvious difference among these four patterns and all the peaks agree with the standard apatite pattern which shows that our precipitates are a pure apatite phase.

Fig. 3 shows the FTIR spectra of samples 1#, 2#, 3#



Fig. 2. XRD patterns of samples 5#, 6#, 7# and 8# prepared at an initial pH = 7.45 in the SBF solution after treated by ultrasonic for 6, 12, 18 and 24 h, respectively.



#### Wavenumber $(cm^{-1})$

**Fig. 3.** FTIR spectra of samples 1#, 2#, 3# and 4# prepared at initial pHs in the SBF solution of 7.15, 7.30, 7.50 and 7.60, respectively, after ultrasonic treatment for 24 h.

and 4#. It can be seen that in sample 1#, only one  $PO_4^{3-}$  band were detected at 1038 cm<sup>-1</sup> compared with sample 4# in which almost all of the  $PO_4^{3-}$  bands are shown in the spectrum. So it can be deduced that the main phase in



Fig. 4. TEM (a) and HRTEM (a) images of typical CAP nano-whiskers. The inset is a selected area electron diffraction (SAED).

sample 1# is CaHPO<sub>4</sub> while only the CAP phase existed in sample 4#. The difference between sample 1# and sample 4# is in accord with their XRD patterns as shown in Fig. 1. In addition, the band at 1450 cm<sup>-1</sup> corresponded to the carbonate group ( $CO_3^{2-}$ ) and indicated that the CAP precipitates contained  $CO_3^{2-}$ , which is similar to the minerals in bone [13].

In order to investigate the detailed morphology and characterization of CAP nano-whiskers, HRTEM images and selected area electron diffraction (SAED) pattern were employed. Fig. 4(a) is a TEM image of CAP nano-whiskers synthesized at an initial pH=7.5 after ultrasonic treatment for 24 h. It can be observed from such images that the biggest length/diameter ratio was more than 20. Moreover, when an HRTEM image in Fig. 4(b) is combined with the SAED (inset in Fig. 4(b)), it could be established that the growth direction of the whiskers was [001]. This result is consistent with the analysis of the XRD patterns.

# Conclusions

In this study, bonelike carbonated apatite nano-whiskers which contained  $CO_3^{2-}$  and had a similar morphology to bone apatite (~100 nm in length and ~20 nm in diameter) were obtained in an SBF solution with ultrasonic assistance.

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