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Kinetic Effects on Hydroxyapatite Whiskers Synthesized by the Chelate Decomposition Method

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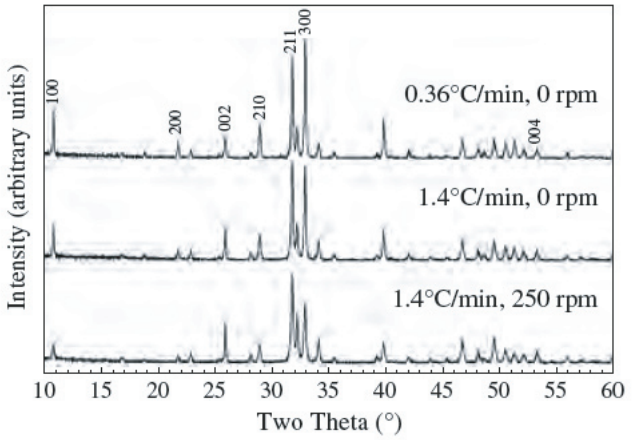

Fig. 1. X-ray diffraction patterns for hydroxyapatite (HA) precipitated at a final temperature of 200°C, which was held for 2 h, showing the effects of selected heating and stirring rates. All reflections correspond to HA.

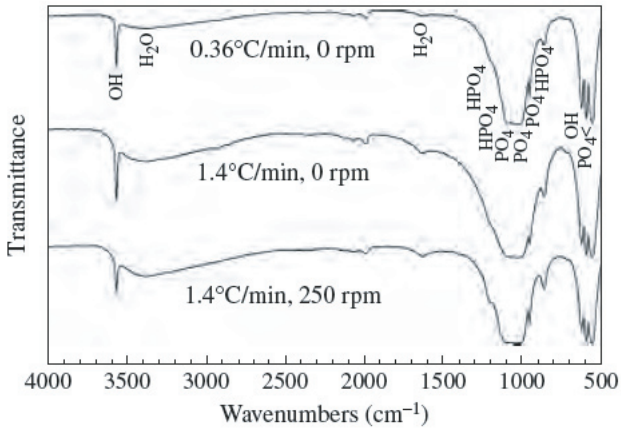

Fig. 2. Fourier transform infrared spectra for hydroxyapatite precipitated at a final temperature of 200°C, which was held for 2 h, showing the effects of selected heating and stirring rates.

Morphology and composition of hydroxyapatite whiskers from reflux-hydrothermal combined treatment using different additives

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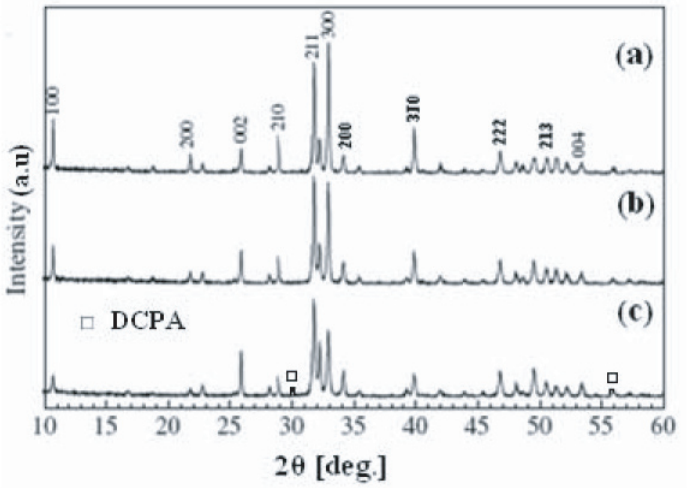

Fig. 1. XRD patterns of as-synthesized precipitates by way of different additives.
(a). urea (b). citric acid (c). Na_2EDTA

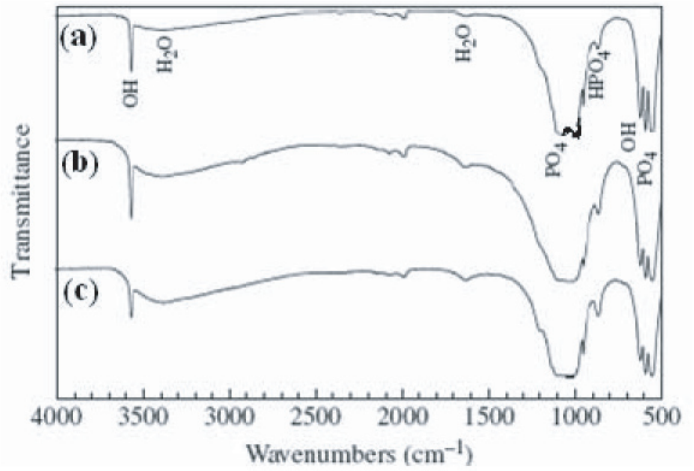

Fig.2. FT-IR spectra of as-synthesized precipitates derived from different additives
(a). urea (b). citric acid (c). Na_2EDTA

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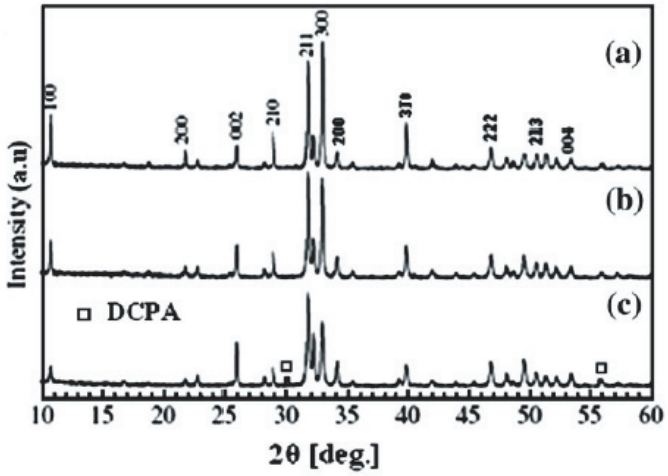

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Abstract

HA whiskers with high crystalline, uniform morphology and high aspect ratio have been successfully synthesized by the reflux-hydrothermal combined method with the aid of urea, citric acid and Na_2EDTA additives. The effects of additives on the whiskers have been investigated in detail. The shape and composition of obtained products were characterized by XRD, FTIR, SEM, TEM and ICP-AES. It is revealed that larger aspect ratios, more uniform morphology, more pure phase composition (Ca/P), shorter reaction time and more mild reaction conditions were reached in contrast to sole reflux or hydrothermal treatment. Urea has the most remarkable effect on the aspect ratio and phase purity of HA whiskers.

Keywords: Reflux-hydrothermal; Hydroxyapatite; Whisker; Characterization methods; Epitaxial growth; Additives

1. Introduction

Hydroxyapatite, with chemical formula of $Ca_{10}(PO_4)_6(OH)_2$ and usually abbreviated as HA, has been verified to be the predominant inorganic constituents of human hard tissues (i.e. bone, teeth and tendon). Actually, natural living bone is a kind of typical inorganic–organic composite consisting of about 70 wt.% of HA and 30 wt.% of collagen matrix [1]. In the bone there exists an inimitable porous structure whose pore diameters distribute from micro to macro range, and in which whisker-or rod-like HA nanocrystals are orderly embedded in collagen matrix. The unique synergy and the hierarchical assembly at the molecular level between HA and collagen matrix endow the living bone with good mechanical properties, such as low stiffness, high resistance to tensile and compressive forces, appreciable flexibility and high fracture toughness [2–5].

The preparation and application of HA materials have progressed fast and greatly in the recent decades. However, dense or porous HA bioceramics constructed by pure synthetic HA powders have a vital disadvantage, i.e., it exhibits very low fracture toughness of about 1 $MPa{\cdot}m^{1/2}$, in contrast to those observed for human bones, which range between 2 to 12 $MPa{\cdot}m^{1/2}$ [6]. In order to overcome the drawback of HA powders, many techniques have been proposed. For example, changing HA powders to whiskers is a quite advisable method. Through controlling suitable synthesizing conditions, the nucleation and growth of HA crystal might be oriented to form different shapes, e.g., powder-like, needle-like, plate-like and rod-like products [7–9]. Hydrothermal treatment and reflux method have been reported to be used in the preparation of HA [10,11]. However, the combination of the two methods is still not found anywhere. Here we firstly report a novel method to synthesize HA whiskers by combining reflux and hydrothermal treatment. Especially, the effects of additives are also investigated in detail.

2. Experimental

2.1. Materials and synthesizing technique

$Ca(NO_3)_2{\cdot}4H_2O$ and $(NH_4)_2HPO_4$ were selected as starting materials to provide Ca and P sources. Disodium ethylene diamine tetraacetic acid (Na_2EDTA), urea and citric acid were used as additives. The above chemicals were of analytical grade and aqueous solutions were prepared by dissolving them into water. A typical procedure was as follows: The designed amount

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of 0.1 mol·l^{-1} $Ca(NO_3)_2$ solution and an additive were added into a three-necked flask with a reflux condenser under nitrogen atmosphere, followed by addition of desired amount of 0.1 mol·l^{-1} $(NH_4)_2HPO_4$ solution dropwise under mild stirring. In the case of urea additive, the pH value of the initial reaction solution was adjusted to round 3 using 0.5 mol·l^{-1} HNO_3. It is noteworthy that the molar atomic ratio of Ca versus P in the incipient solution was adjusted at 1.67, which is equivalent to that of stoichiometric HA. The reaction solution were then heated and refluxed at 353.15–363.15 K for 3–4 h so as to ensure the complete mix and reaction.

On finishing the reflux process, the product in the distillatory was carefully transferred into a teflon-lined pressure vessel purged with nitrogen, sealed tightly and heated with a rate of 273.65 K·min^{-1}. Under the final temperature of 423.15–473.15 K and pressure of 3–4 MPa, the hydrothermal treatment time was held for 2 h. After completion of the hydrothermal reaction, the vessel was naturally cooled down to room temperature with the air. The as-synthesized precipitate was totally collected, suction-filtered and washed with water and ethanol. The solid product should be dried at 353.15 K for 24 h at least. In order to study the effect of additives, the pH value of the supernatant solution before and after reflux and hydrothermal treatment was measured using a pH meter.

2.2. Characterization of the whiskers

The size and shape of as-synthesized whiskers were observed and measured quantitatively using SEM and TEM, and the aspect ratio (length/width) was calculated. The compositions of the whiskers were determined by XRD and FTIR. The calcium and phosphorus element contents of the whiskers were measured by ICP-AES and spectrophotometer, respectively, so as to compare the precision of the measuring methods.

3. Results and discussion

3.1. Identification of the whiskers

It is clearly shown in Table 1 that the additives have great effect on the shape and composition of the whiskers. At the initial stage of reflux, all the solutions were homogeneous, colorless and acidic (pH < 5.0). After the reflux and hydrothermal treatment, the color of supernatant solutions containing the citric acid and Na_2EDTA turned faint yellow and red, respectively, but the color with urea still kept colorless. Their final pH values after hydrothermal treatment rose remarkably except for little rise for the citric acid case, suggesting the formation and decomposition of the Ca complexes. More importantly, relatively large-sized HA whiskers could be obtained in contrast to separate use of reflux or hydrothermal method. Meanwhile, The HA whiskers bearing lower Ca/P ratios (relative to 1.67 for stoichiometric HA) under the condition of three additives were obtained, indicating the formation of calcium-deficient HA whiskers to some extent.

Table 1
As-synthesized whiskers derived from different additives

	pH				Ca/P ratio	Aspect ratio	Phase composition
	Reflux		Hydrothermal				
	Initial	Final	Initial	Final			
Urea	2.64	5.59	5.61	5.97	1.65	~70	HA
Citric acid	2.63	3.24	3.25	3.66	1.63	~50	HA, OCP*
Na_2EDTA	4.98	5.79	5.80	5.89	1.59	~40	HA, OCP, DCPA*

OCP*: $Ca_{(10-x)}(HPO_4)_x(PO_4)_{(6-x)}(OH)_{(2-x)}$ $(x \le 1)$.
DCPA*: $CaHPO_4$.

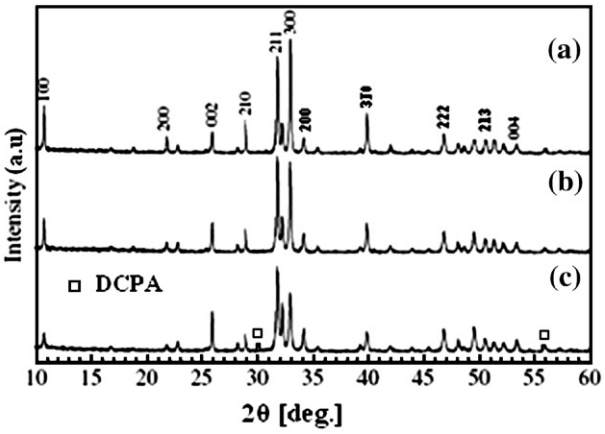

Fig. 1. XRD patterns of as-synthesized precipitates using different additives. (a). urea (b). citric acid (c). Na_2EDTA.

The XRD patterns in Fig. 1 could be indexed on the basis of a hexagonal unit cell with $a=b=0.9424\pm0.0002$ nm and $c=0.6879\pm0.0004$ nm which are typical values for HA crystals. In the Fig. 1 (c) two quite weak peaks were observed, denoting the existence of little amount of monetite (DCPA). However, our further investigation revealed that the DCPA could transform to HA when the hydrothermal treatment time exceeds 4 h. Likewise, the FTIR spectra of the whiskers also clarify that there are characteristic peaks in HA corresponding to PO_4^{3-} (560–600 cm^{-1}, 1030–1090 cm^{-1}) and OH^- (630 cm^{-1}, 3570 cm^{-1}) groups in the structure, but no obvious CO_3^{2-} absorption peak was found, probably resulting from the nitrogen protect during the experimental process. The SEM image in Fig. 2 exhibits that the HA whiskers possess comparatively uniform shape and size, especially the largest aspect ratio of 70 in the case of urea. Under the case of citric acid and Na_2EDTA additives, the aspect ratios are slightly smaller, but still larger than that obtained by separate hydrothermal or reflux method.

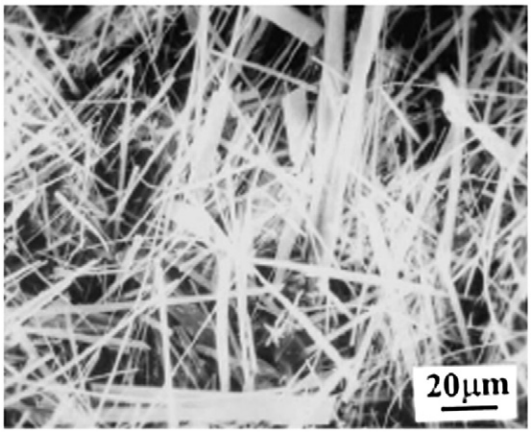

Fig. 2. The SEM image of as-synthesized whiskers with the help of urea additive.

3.2. Effects of the additives on the morphology and composition of the whiskers

Citric acid and Na_2EDTA are carboxylic acid and its salt, respectively, and easily ionized to carboxylic group when dissolved in water. Carboxylic group can react with Ca^{2+} to form Ca-complexes. With the proceeding of reaction, the Ca-complexes decompose and calcium ion is slowly and uniformly released into the phosphate-containing solution, and calcium phosphate crystals nucleate and grow. Urea decomposition takes advantage of an increase in solution pH caused by the slow hydrolysis of urea in aqueous solutions [12]. In acidic homogeneous solutions or suspensions, calcium phosphate precursors such as DCPA appear at pH=2–4 where HA is instable. With the gradual hydrolysis of urea, the solution pH will rise above 4, where HA is stable, and HA crystals nucleate by dissolution and reprecipitation from calcium phosphate precursors and/or intermediate phases [13]. During the reflux and hydrothermal treatment, DCPA and OCP gradually change into HA according to different reaction routes [14]. The fibrous OCP with calcium-deficient HA formula of $Ca_{(10-x)}(HPO_4)_x(PO_4)_{(6-x)}(OH)_{(2-x)}$ ($x \leq 1$) provides the formwork for the growth of HA whiskers, and HA whiskers are hereby formed by the epitaxial overgrowths [15]. With the rise of the pH and duration, the Ca^{2+} vacancies in the OCP will absorb Ca^{2+} ions, which gradually drives calcium-deficient HA whiskers to transform to the stoichiometric HA. This can also be reasoned out from that the intensity of FTIR bands for hydroxyl and HPO_4^{2-} group were found to increase and decrease, respectively, with the increase of duration.

The reflux-hydrothermal technique combines the advantages of both the methods. First, reflux is helpful to well-proportioned mixing of reactants, and formation of calcium phosphate precursors under relatively mild conditions due to its kinetic action. Secondly, hydrothermal treatment can provide a uniform, static and high-pressured micro system for the decomposition of Ca-complex and the hydrolysis and reprecipitation of calcium phosphate precursors. Owing to the similarities of the structure, composition of OCP and HA, the stoichiometric HA whiskers can be slowly formed by the controlled hydrolysis of the precursor and thus take over the shape of fibrous OCP.

4. Conclusion

HA whiskers with high crystalline, uniform morphology and high aspect ratio could be successfully synthesized by the reflux-hydrothermal combined method with the aid of three different additives under relatively mild synthetic conditions and shorter time. Under the given reaction conditions, urea additive has the largest effect on the improvement of shape and size of HA whiskers in the three additives and the mean aspect ratio can reach about 70. Moreover, the Ca/P ratio of 1.65 is rather close to stoichiometric HA, implying the inexistence of other phase-impure apatite. The citric acid and Na_2EDTA can similarly play a remarkable role in the preparation of HA whiskers using the same technique.

Acknowledgments

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