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The precipitation of three Ca-P phase whiskers from an acid solution through hydrolysis of urea

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Hydroxyapatite (HA), beta-tricalcium phosphate (β-TCP) and dicalcium phosphate (DCP) whiskers with high aspect ratio and good crystallinity were successfully prepared by hydrolysis of urea in acid solutions at 90°C for 96 h. The precipitated whiskers were characterized by XRD, SEM and TEM. The lengths and aspect ratios of whiskers could be controlled by the precipitation agent, urea, with a proper incubation time. Results revealed good morphology and crystallinity of the precipitated whiskers without any impurities. TEM indicated single crystal diffraction patterns of HA and β-TCP were clearly identified. The high aspect ratio of whiskers could be potentially used as the scaffold in tissue engineering or filler in composite biomaterials to enhance mechanical properties.

Key words: Whisker; Hydroxyapatite (HA), Beta-tricalcium phosphate (β-TCP), Dicalcium phosphate (DCP).

Introduction

Research on whiskers has already made significant contributions to the fields of crystal growth and strength of composite materials [1, 2]. Whiskers are required in the development of modern composite materials, particularly in reinforced composites based upon polymers, metals and ceramics. A whisker can improve the fracture toughness and strength of a ceramic or a polymer matrix composite, which can be extensively used in the biomedical fields [3, 4], because of their small dimensions and high elastic strength. Therefore, whiskers are undoubtedly of continuing interest for researchers.

Calcium phosphate bioceramics (Ca-P), one type of bioactive material that can form a direct bond with bone, have been used in biomedical engineering for nearly 20 years. Due to their excellent biocompatibility, bioactivity and osteoconductivity, they have been widely applied in the hard tissue area [5, 6], including dental implants, periodontal treatment, orthopedics, bone graft substitute and maxillofacial surgery [7, 8]. At present, applications for calcium phosphate bioceramics are restricted to areas free of dynamic load bearing because bioceramics are known for their brittleness. Fortunately, whiskers can be expected to be applied to these fields, for example, the scaffold for tissue engineering, as whiskers can be used to enhance the mechanical properties of highly porous materials.

Among calcium phosphate bioceramics, hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) has been recognized as the most important of bioceramics, as it is considered as the major inorganic component of natural bone. Another Ca-P phase, beta-tricalcium phosphate (β-TCP, $Ca_3(PO_4)_2$), has also attracted extensive interesting research due to its biodegradation.

Various methods for preparation of such ceramic materials are well established including solid-state reactions [9], wet chemical reactions [10, 11] and hydrothermal treatments [12-14]. Although there have been a large amount of research on calcium phosphate crystal growth, modulating the Ca-P growth under a controlled environment remains as a challenging issue [15]. Various types of factors in the preparation conditions have important effects on the morphology of whiskers. Various methods have been employed to control crystal growth and synthesize crystals with different morphologies, such as a microwave and hydrolysis reaction [16], wet chemical synthesis [17-19] and hydrothermal methods [20].

In recent reports [20, 21], it was found that urea can be used to control the Ca-P crystal growth through the pH value variation caused by its hydrolysis [22]. Further, the pH value was one of the most critical factors affecting the Ca-P growth. In this paper, we report a synthesis method of calcium phosphate whiskers through urea hydrolysis. This method is advantageous because the results demonstrate that pure and homogenous whiskers with good crystallinity without any other impurities can be synthesized and the preparation process was simple and easy to control. In this study, HA, β-TCP and dicalcium phosphate (DCP, $CaHPO_4$) whiskers that is another type of bioactive ceramic were prepared by hydrolysis of urea. The crystalline phases and morphology of the three whiskers were identified by X-ray diffractometry (XRD) and scanning electron microscopy (SEM), respectively. The microstructure of single crystal whiskers

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was investigated by transmission electron microscopy (TEM).

Experimental procedures

Reagent-grade $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$ (Kelong Chemicals Co., Chengdu, China) were used as starting materials for the fabrication of HA, β-TCP and DCP. The typical experimental procedures were as follows: calcium ions and phosphate ions were prepared by dissolving analytical grade reagents $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$ in distilled water. To prepare the different Ca-P whiskers, different stoichiometric Ca/P molar ratios were prepared by mixing the desired amounts of calcium ion and phosphate ion solutions. The preparation conditions are detailed in the Table 1. The starting pH value could be changed by adding 0.5 mol/l HNO_3 to achieve the desired value. After mixing the three solutions, they were put into a triangular flask together with the desired amount of additive, urea (0.1 mol/l), at 90°C for 96 h. After the reaction, the solid product was filtered and washed with distilled water, followed by an ethanol treatment to remove the residual ions and water. Finally, whiskers were dried at 80°C in a vacuum oven.

Crystalline phases of whiskers were identified by X-ray diffractometry (XRD, X'Pert, Holland). The morphology of the precipitated whiskers was observed with a scanning electron microscope (SEM, JSM-5900LV, Japan). The average length and aspect ratio of whiskers were determined by randomly sampling 25-35 whiskers in a SEM micrograph. Transmission electron microscopy (TEM) was used to investigate the microstructure of single crystals of whiskers. The crystal sample was dispersed in ethanol and placed on a copper mesh for TEM observations.

Results and Discussion

The morphologies of the HA, β-TCP and DCP were observed through SEM. SEM observations show that the length of HA is around 4-15 μm while the width ranges from 0.2 to 2 μm as shown in Fig. 1a. The longest whiskers could be as long as 17 μm. The aspect ratio of HA whiskers could be as large as 20-50. It is interesting to note that the morphologies of the β-TCP whiskers are different. β-TCP is composed of small plates that contact each other tightly (Fig. 1b). The length of β-TCP whiskers is around 5-10 μm while the width ranges from 0.5-1 μm. The aspect ratio of β-TCP whiskers could be as large as 10, which is smaller than that of HA. Fig. 1c shows the morphologies of DCP whiskers, which are around 30-60 μm in length and 0.5 μm in width. The aspect ratio ranges from 60-120.

The variety of length and width of three calcium phosphate whiskers may be due to the different rate of Ca-P crystal growth during the precipitation process. By selecting the synthetic conditions, it is possible to obtain whiskers with different aspect ratio with a desired shape and size. The precipitation of calcium phosphate from aqueous solutions is somewhat complicated due to the possible occurrence of several solid phases depending on the solution composition and the pH. When the pH is low (pH < 4.3), the DCP phase is the

Table 1. The preparation conditions of three whiskers.

Whisker	Ca/P ratio	Initial pH	Final pH
HA	1.67	4.3	6.2
β-TCP	1.5	4.5	6.7
DCP	1	4	6.1

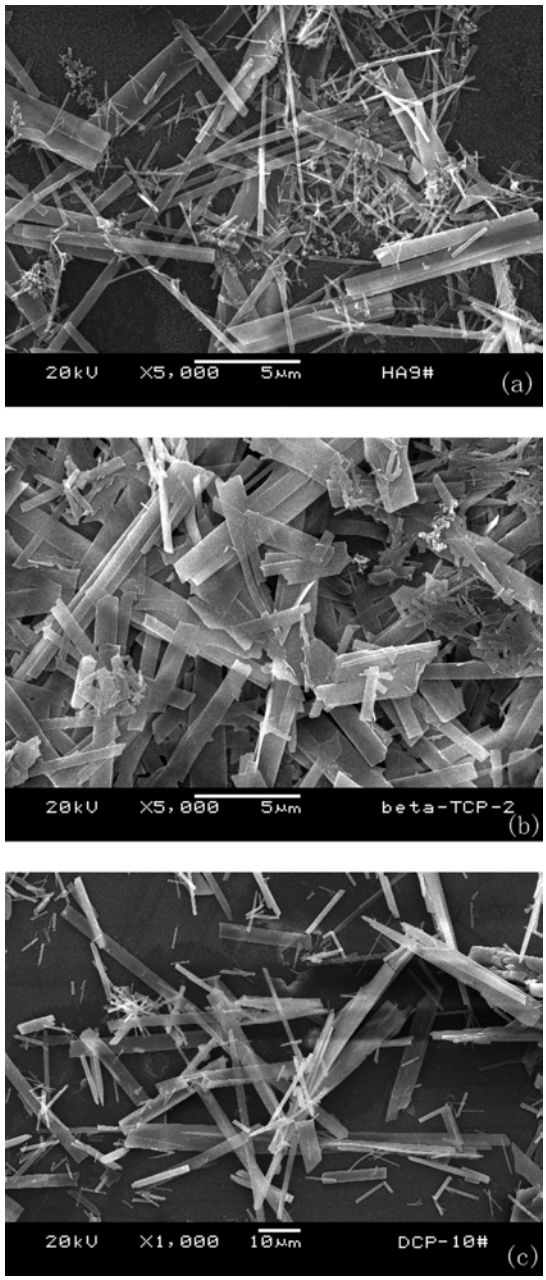

Fig. 1. The morphologies of whiskers: HA(a), β-TCP(b) and DCP (c).

stable phase. When the pH ranges from 4.8-8, the solubility of HA, β-TCP and DCP are often in the order DCP ≫ β-TCP ≫ HA [23]. With the hydrolysis of urea, the pH value of the solution is raised. As soon as a critical pH value is obtained, the solid phase will precipitate. Further, when the processing time increases, the length and width of whiskers will increase. Fig. 2a shows that DCP whiskers become longer after 144 h than those prepared after 96 h, and some new small whiskers formed endlessly (Fig. 2b). The small whiskers formed indicate a nanorod morphology as shown in the inserted micrograph in Fig. 2b. Interestingly, when no urea was added into the starting solution that was needed for preparing DCP whiskers, no whiskers could be obtained after 144 h, but tadpole-like shaped precipitates were obtained from the solution without the addition of urea. The morphology of the obtained precipitates is shown in the Fig. 2c. It can be seen that the trend of forming whiskers has almost ceased. As long as a driving force was introduced, the precipitates would continue to grow and eventually formed whiskers.

The crystal phase of the precipitated whisker was investigated by XRD. XRD analysis (Fig. 3) reveals that HA crystals whiskers exhibited distinct diffraction

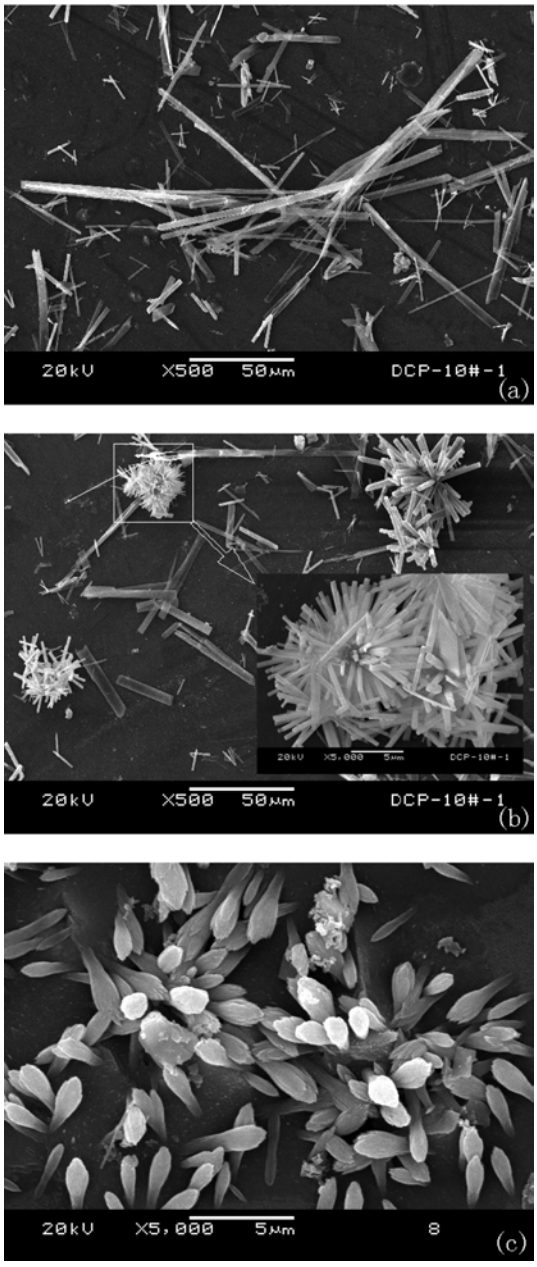

Fig. 2. The morphologies of DCP whiskers (a) after 144h, the magnification morphologies of local view (b) and the morphology of precipitates without urea after 144h (c).

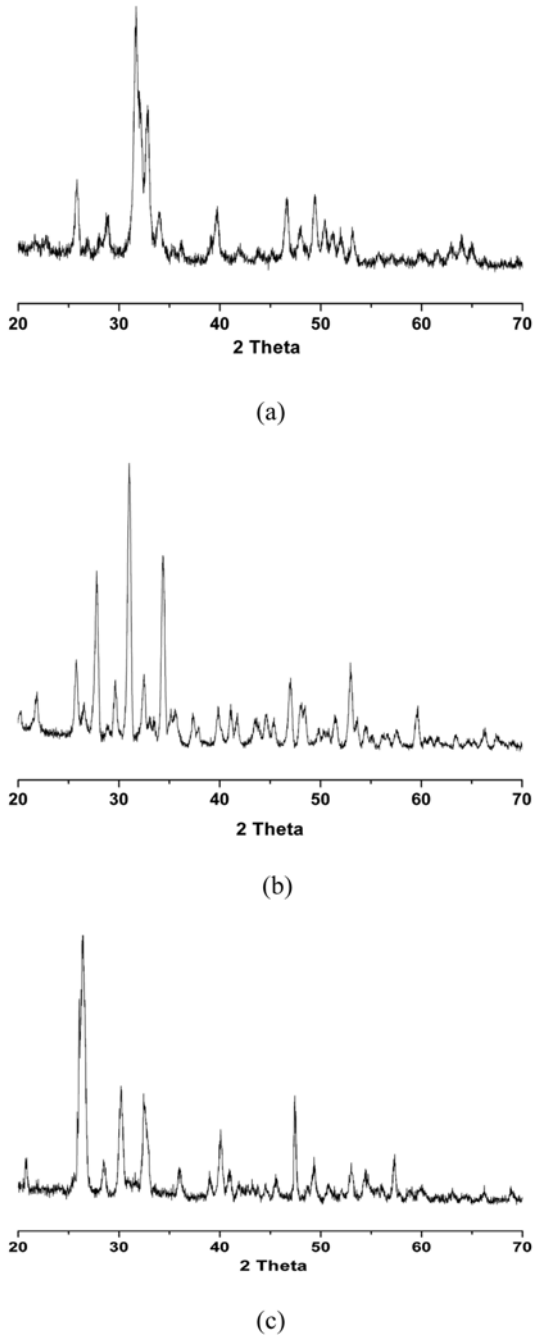

Fig. 3. The XRD patterns of three whiskers: HA(a), β-TCP(b) and DCP (c).

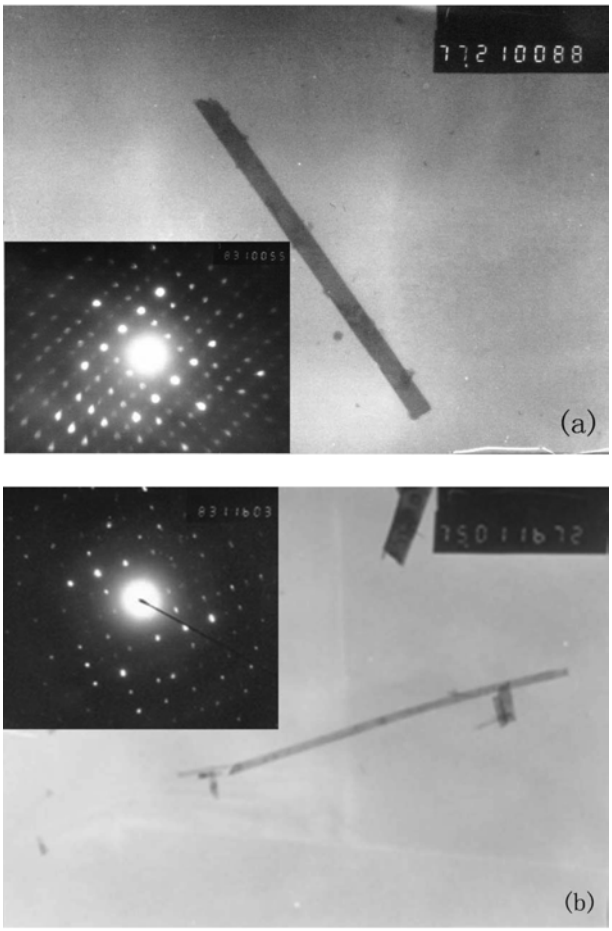

Fig. 4. TEM micrographs and SAD patterns:(a)HA whisker, (b) β-TCP whisker.

peaks at 2θ 25.88, 31.77, 32.20, 32.90, 39.82, 46.71 corresponding to the d 3.440Å (002), d 2.814Å (211), d 2.778Å (112), d 2.720Å (300), d 2.262Å (310), d 1.943Å (222) crystal planes of HA. These peaks are consistent with the characteristic peaks of crystallized HA as listed in JCPDS card (PDF#09-0423). The XRD spectra of β-TCP crystals exhibits diffraction peaks at 2θ 27.77, 29.66, 31.03, 32.45, 34.37 corresponding to the d 3.210Å (214), d 3.010Å (300), d 2.880Å (0 2 10), d 2.757Å (128), d 2.607Å (220), which are consistent with the spectra of typical β-TCP (JCPDS PDF#09-0169). The Fig.3c shows all the typical DCP diffraction peaks at 2θ 26.43, 30.19, 32.89 corresponding to the d 3.370Å (020), d 2.958Å ($\bar{1}$ 12), d 2.721Å (102) crystal planes of DCP (JCPDS PDF#09-0080). From the above results, it could be seen that the whiskers obtained by this method have good crystallinity and high purity.

The orientation and crystal structure of an individual HA and β-TCP whisker were further examined by TEM and selected area diffraction (SAD). Fig. 4a and 4b present the typical bright field images and SAD results of a single crystal HA whisker and single crystal β-TCP whisker. The diffraction patterns of the whiskers indicate only one orientation, which proves that the obtained whiskers are single crystals. TEM examinations present hard evidence that well-crystallized whiskers can be obtained from this reaction route.

Conclusions

In this study, well-crystallized pure HA, β-TCP and DCP whiskers were successfully produced. The experimental results revealed that using urea hydrolysis to control the crystal growth process was an effective way of fabricating single crystal HA, β-TCP and DCP whiskers without any impurities, and that the pH value was the critical factor affecting the crystal growth process after fixing the Ca/P ratio condition. The high aspect ratio of whiskers could potentially be used as the scaffold in tissue engineering or as a filler in composite biomaterials to enhance mechanical properties.

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