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Synthesis of carbonated hydroxyapatite nanofibers by mechanochemical methods

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Abstract

Carbonated hydroxyapatite nanofibers were prepared via a reaction among $CaHPO_4{\cdot}2H_2O$, $CaCO_3$ and urea aqueous solution by mechanochemical method. The nanofibers were 50–150 nm in length and ~8 nm in diameter, respectively. The microstructure and characteristics of the resultant nanofibers were studied by means of X-ray diffraction (XRD), transmission electron microscopy (TEM), infrared spectrometer (FTIR) and thermogravimetric analysis (TG-DSC). It has been found that hydroxyapatite nanofibers have high crystalline and fairly pure phase.

Keywords: Mechanochemical synthesis; Carbonated hydroxyapatite; Nanofiber

1. Introduction

Because of compositional and biological similarity to native tissues, hydroxyapatite (HAp) is one of the most attractive materials for vertebrate and dental implants. Hydroxyapatite (HA) sometimes refers to calcium phosphate tribasic phase and has the chemical formula $Ca_{10}(PO_4)_6(OH)_2$. The Ca^+, PO_4^{3-} and OH^- ions can be replaced by other ions during processing or in physiological surroundings; e.g., fluorapatite ($Ca_{10}(PO_4)_6(OH)_{2-x}F_x$, with $0 < x < 2$) and carbonate apatite ($Ca_{10}(PO_4)_6(OH)_{2-2x}(CO_3)_x$ or $Ca_{10-x+y}(CO_3)_x(PO_4)_{6-x}(OH)_{2-x+2y}$, where $0 < x < 2$ and $0 < y < x$) can be formed [1,2]. Among the variety of HAp-based materials, carbonated HAp appears to be an excellent material for bioresorbate bone substitutes. Recent in vivo study indicated that the dissolution rate of sintered carbonated HAp ceramics implanted subcutaneously was intermediate between tricalcium phosphate (β-TCP)and pure HAp [3]. These studies suggest that carbonated HAp materials should be superior to pure HAp for bioresorbable implants. However, the relatively low strength and susceptibility to brittle fracture of the HAp-based materials have severely limited its use to only non-loadbearing application [4,5]. It is well known that fibers are widely used to improve the strength and fracture toughness of brittle materials. Therefore, many synthesis techniques for carbonated HAp fibers with low crystallinity and suitable size have been developed, such as hydrothermal synthesis, homogenous precipitation, solid synthesis at high temperature and growth in the gel system [6–8]. Generally, the diameters of these produced fibers are large in the range from 0.1 to 10 μm. This would lead to break easily in the processes of preparing ceramics.

Nanofibers with the aspect ratio and physical shape mimic the crystalline hydroxyapatite structure [9] of natural bone (i.e., hydroxyapatite crystal dimensions from 50–100 nm in length and 1–10 nm in diameter). Moreover, the theoretical prediction for strength and flexibility of materials made from nanofibers such as carbon nanofibers is much higher than those prepared from general powders. We believe that the HAp nanofibers would have great potential for use as biomaterials in medical fields.

Our earlier works on HAp synthesis showed that carbonated HAp powder can be easily obtained by mechanochemical method, whose composition is similar to native

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hard tissues. The main advantage of this method is simplicity and low cost. In the present work, urea is selected as additive for its slow hydrolyzation, which makes pH value increase steadily, and keeps a low supersaturation that is required for crystal growing during the processing of mechanochemical synthesis of hydroxyapatite-based nanofibers.

2. Experimental

The starting materials selected in this experiment were dicalcium phosphate dihydrate ($CaHPO_4{\cdot}2H_2O$) and calcium carbonate ($CaCO_3$) powders. The materials were weighed to coincide the stoichiometric HAp. A planetary ball mill containing 150 g zirconia balls of 10–15 mm diameter was used for grinding the mixtures. The mixture powder (50 g), distilled water (105 ml) and urea were put in the mill and ground at 1000 rpm. During the grinding, the milling was periodically stopped and 5 ml of aqueous suspension was removed for further analysis. The obtained powders were submitted to X-ray diffraction (D/MAX-2500) and to infrared spectrometric analyses (Nicolet 5DX). The ground mixtures were also subjected to thermogravimetric and differential thermal analysis (TG-DSC, NETZSCH STA499C) simultaneously at a heating rate of 10 °C/min. The morphology of the synthesized powders was observed by Hitachi-800 transmission electron microscope (TEM).

3. Results and discussion

3.1. Phase evolution

The XRD patterns of the powders obtained after grinding for different time are shown in Fig. 1. After 30 min of grinding, the principal diffraction lines corresponding to $CaHPO_4{\cdot}2H_2O$ and $CaCO_3$ disappeared and most of the starting materials convert to amorphous phase. Simultaneously, the low crystallinity of HAp, with XRD spectra that exhibit broadened and weak peaks situated at 2θ angles of 25.82° and ~31.76°, is formed in the ground mixture. This suggested that the mechanochemical reactions proceed in the aqueous system when the interfaces of solid surfaces were closely contacted and sheared by grinding. The mechanochemical method is based on the deep squeezing and crushing of powder in the limited surface area of the spherical segment adjacent to the contact point of zirconia milling ball on the container wall. The physical–chemical condition needed to shift a chemical reaction towards the required products can be the change of two fundamental parameters: temperature and pressure. The pressure arises mainly by the load coming from gravity force of all the zircoina balls and the centrifugal force. At high pressure, the crystal structures of DCPD containing sheets of composition –Ca–PO_4–Ca–PO_4– collapse in the plane of the sheet as the

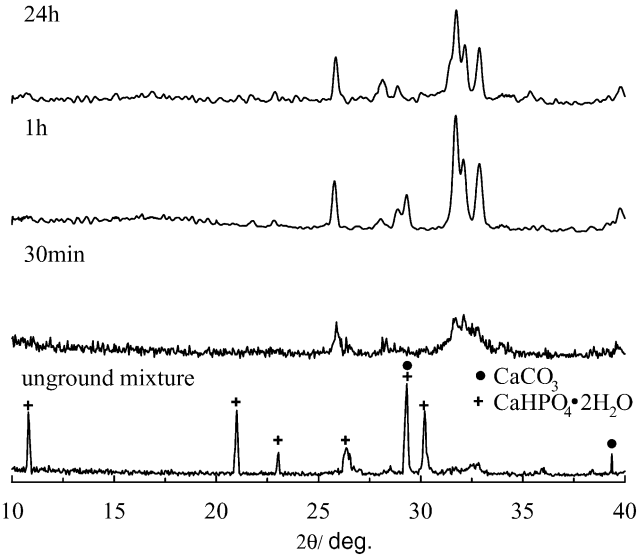

Fig. 1. XRD patterns of the powders obtained after grinding for different time.

transition from crystalline to amorphous takes place. Similarly, the pressure also induces crystalline to amorphous transitions in $CaCO_3$. Therefore, the ground mixture appears amorphous. Meanwhile, high temperature (up to 450 °C) of local zones can be formed due to friction effects and adiabatic heating of CO_2 gas bubbles, while the over all temperature is relatively low (after grinding 24 h, the slurry temperature ranged between 48 and 54 °C). This would accelerate kinetic processes, such as dissolution, diffusion, reaction rate and nucleation and growth (crystallization from amorphous state). On the other hand, alkaline environment of the synthesis caused by the hydrolyzation of urea is very important because higher pH values favor formation of apatite phase [10]. As the grinding time was increased to 1 h, only those diffraction lines belonging to the HAp can be detectable, which indicated that the synthesis reaction was greatly enhanced. Further increasing the grinding time to 24 h, no noticeable changes were observed, except the peaks broadening and overlapping to some extent. This can be explained by the formation of some non-spherical particles (nanofibers) and a decrease of crystalline due to increased carbonate substitution in the HAp lattice [11]. However, it is not possible to exclude the presence of other calcium phosphate–carbonate compounds in the amorphous state, which are not detectable by XRD analysis.

3.2. Morphology and characteristics of HAp nanofibers

Fig. 2 showed TEM imagine of mixture powder after grinding for 24 h. It was estimated that the nanofibers were 50–150 nm in length and ~8 nm in width. The FTIR spectrum of the mixtures is given in Fig. 3. Most of the bands, which appeared in the range of analysis, can be attributed to a carbonate HAp containing water. The absorption bands at 1087, 1046, 962 and 576 cm^{-1} detected in the spectrum are

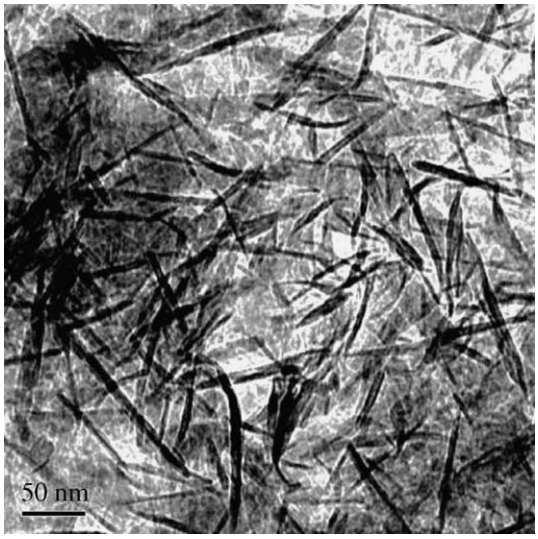

Fig. 2. TEM micrograph of the mixture powder after grinding for 24 h.

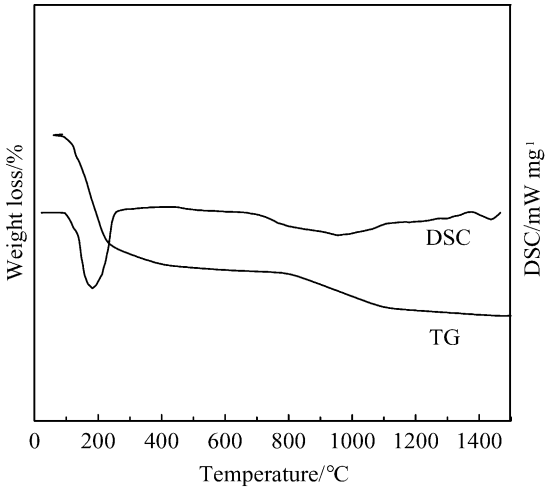

Fig. 4. TG-DSC curves of the as prepared carbonated HAp powders.

attributed to the PO_4^{2-} in hydroxyapatite. The absorption bands at 1419 and 875 cm^{-1} suggest the presence of CO_3^{2-} and the bands at 630 cm^{-1} and 3572 cm^{-1} are assigned to the OH^-. The presence of CO_3^{2-} ions in the infrared spectra indicates that the hydroxyapatite formed during the mechanochemical reaction includes some carbonate-substituted apatite and is not stoichiometric apatite. The broadening of the PO_4^{3-} bands and the low intensity of OH^- bands might be caused by a decrease of crystallinity due to substitution of CO_3^{2-} for PO_4^{3-} or CO_3^{2-} for OH^- in HAp powder. However, it is difficult to distinguish correctly CO_3^{2-} in PO_4^{3-} position from CO_3^{2-} in OH^- position.

TG-DSC curves of the as-prepared carbonated HAp powders in the temperature range of 50–1460 °C are shown in Fig. 4. An obvious weight loss of 4.5% was detected up to approximately 400 °C and was due to the loss of absorbed and lattice water [12]. The second endothermic trend took place between 780 and 1130 °C, which is attribute mostly to the decarbonation and dehydroxylation. The total weight loss is about 2.2%. No other endothermic change and weight loss occurred in the range of 400–780 °C. If the as-prepared HAp powders contain some unreacted $CaCO_3$, it would produce rapid weight losses at 400–780 °C, but not a platform that appeared in the TG curve. This implies that there is no unreacted $CaCO_3$ existing in amorphous phase and the synthesized carbonated HAp nanofibers is pure.

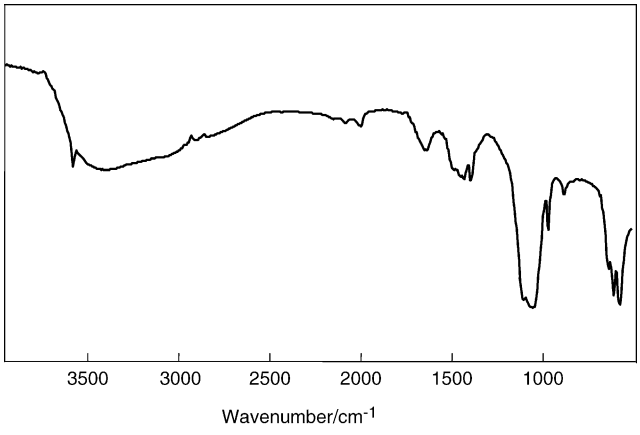

Fig. 3. FTIR spectrum of the mixture powder after grinding for 24 h.

4. Conclusion

1. Carbonated hydroxyapatite nanofibers was synthesized by grinding of $CaHPO_4{\cdot}2H_2O$ and $CaCO_3$ mixture in an aqueous system containing urea. The hydrolyzation of urea played an important role to favor crystalline of HAp nanofiber.
2. The synthesis reaction was almost completed within 1 h.The length of the typical nanofibers is about 50–150 nm and the diameter is about 8 nm.

Acknowledgements

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