Microwave-assisted solid-state synthesis of hydroxyapatite nanorods at room temperature

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Hydroxyapatite (HAP) is the main inorganic constituent of human hard tissues, such as bones and teeth [1]. HAP is usually used in various physical forms such as granules, rods and coating over metallic implants. For example, Bone itself is a composite with HAP nanorods embedded in the collagen matrix [2]. HAP is commonly employed as a coating for bioinert metallic and ceramic substrates, such as titanium and alumina [3, 4]. Dense HAP ceramics can serve as bone substitution, which require their good mechanical properties. Therefore, especially required is the HAP powders which exhibit desired characteristics such as small grain size with narrow size distribution and high specific surface area.

According to the previous literatures, a number of methods have been proposed for preparing HAP, such as wet chemical routes based on precipitation at low temperature [5, 6], hydrothermal methods [7, 8] and solid-state reactions [9] etc. The wet chemical methods usually lead to irregular forms of HAP powders and require complex process control. In recent years, the hydrothermal routes towards the synthesis of HAP nanorods have been reported [7, 8]. In spite of its much particular characters in high-temperature and high-pressure conditions, the hydrothermal synthesis route is relatively complex and reaction time is comparatively long. So some attentions have been switched to seek some new methods. The high-temperature solid-state method has been applied to the synthesis of HAP for the past several decades [9]. Due to its too much energy consumption, complex apparatus and techniques, the solid-state reaction becomes gradually unpopular and unsatisfied. At present, there are many compounds which have been synthesized by solid-state reaction at room temperature, such as oxide, sulfide, carbonate, hydroxide and so on [10–13]. However, the synthesis of HAP nanorods at room temperature is seldom reported until now. Recently, it is reported that HAP nanoparticles have been synthesized by microwave-mediated metathesis in room temperature solid-state reaction [14]. Unfortunately, the products obtained only took the form of particles with large size and irregular diameter distribution. Microwave irradiation has particular advantages such as rapid volumetric heating, high reaction rates, leading to products with small particle sizes, narrow size distribution, and high purity [15]. Thus, in our work, microwave heating as an important processing method was first introduced to the synthesis of HAP by solid-state reaction at room temperature.

Calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) and tri-sodium phosphate ($Na_3PO_4{\cdot}12H_2O$), according to stoichiometric ratio (1.67) were used as starting materials. They were ground for 5 min respectively followed by milling the mixture at room temperature for 20 min. We did four groups of parallel experiments (group 1: microwave heating for 0.5 min, on for 15 s and off for 15 s; group 2: microwave heating for 1 min, on for 15 s and off for 15 s; group 3: conventional heating at 80 °C for 6 hr in oven; and group 4: continuous microwave heating for 1 min). The as-prepared products were transferred into Teflon vessels and then were respectively put into a conventional oven and a domestic microwave oven (LG, MS-2079 T, 2.45 GHz, 700 W) whose 30% of the output power was used to irradiate the mixture. The resultant products were washed with ethanol and distilled water respectively for several times to remove unreacted ions, namely Na^+, NO_3^-. And then the precursor was dried in an oven at 80 °C for 6 hr.

The above products were collected for the characterization of powder X-ray diffraction (XRD) (Bruker D8 advance), field-emission scanning electron microscope (FE-SEM) (LEO1530), transmission electron microscopy (TEM) (JEOL, JEM-200CX, at 200 kV) and fourier transform-infrared (FTIR) spectrophotometry (NICOLET 510P).

The XRD patterns of the synthesized HAP are presented in Fig. 1. From Fig. 1c we can observe that, the products obtained under conventional heating mode for 6 hr was poorly crystallized, while well-crystallized products of HAP are easy to be obtained when microwave heating Fig. 1a, b, and d was employed. The peaks of XRD patterns in Fig. 1a, b, and d are consistent well with the hexagonal HAP crystal. The relatively wider peaks in Fig. 1a suggest that the products would have relatively smaller sizes, as proved by SEM image later (Fig. 3a and b).

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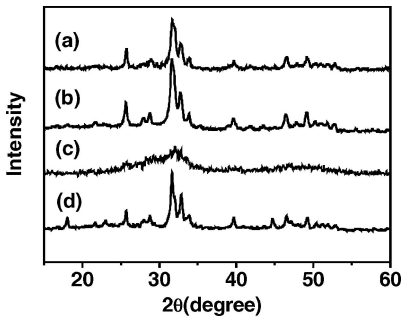

Figure 1 Wide-angle XRD patterns of synthesized hydroxyapatite (HAP) samples at different heating modes: (a) microwave interval heating for 0.5 min; (b) microwave interval heating for 1 min; (c) conventional heating for 6 hr (80 °C); (d) microwave continuous heating for 1 min.

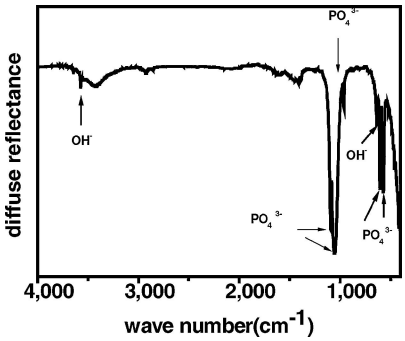

Figure 2 FT-IR spectra of the synthesized HAP sample using microwave interval heating for 1 min.

Fig. 2 shows the FT-IR spectra of the HAP nanorods employing microwave heating for 1 min. The spectra indicate the presence of OH^- and PO_4^{3-} in the resultant samples. For example, bands at 603 and 573 cm^{-1} due to $v_4PO_4^{3-}$ in crystalline HAP. Peaks at 964 cm^{-1} reflect $v_1PO_4^{3-}$ and 1091/1052 cm^{-1} for $v_3PO_4^{3-}$. The band attributing to the stretching vibrations of OH^- ions appears at 3574 cm^{-1}, and the 635 cm^{-1} band is due to the vibration motion of the OH^- ions [16].

Fig. 3 shows the morphology and size distribution of the prepared samples at different conditions. We can see from the SEM images (Fig. 3a and b) the HAP nanoparticles were obtained using microwave heating for 0.5 min. However, as the microwave heating time was increased to 1 min, the HAP nanoparticles transformed into nanorods with diameters varying from 60 to 80 nm and an average length of about 400 nm (Fig. 3c). From this image we can also see, the HAP nanorods possess uniform morphology with roughly same aspect ratio. Comparing Fig. 3a and b with Fig. 3c, we can conclude that microwave heating time plays an important role in the formation of HAP nanorods. The HAP samples imaged by Fig. 3d mainly consist of short rod-like structures with lower aspect ratio.

The results above show that HAP nanoparticles and nanorods with different sizes have been prepared successfully. Obviously, HAP cannot be obtained without microwave heating (Fig. 1c). If microwave heating was introduced into this solid-state reaction, HAP could be prepared easily. Also the HAP crystals with different morphologies (Fig. 3a and c) can be prepared by varying the microwave heating time. The interval time of microwave heating has also very important influence on the structure and size of HAP. We can draw the conclusion that continuous microwave heating can lead to the large sized nanorods of HAP compared with the interval heating method (Fig. 3c and d). It is generally known that solid-state reaction usually requires harsh reactive conditions such as high temperature or high pressure, because of its too much block and low diffusivity of molecules or atoms of crystal lattice. That is probably why we did not obtain products in the

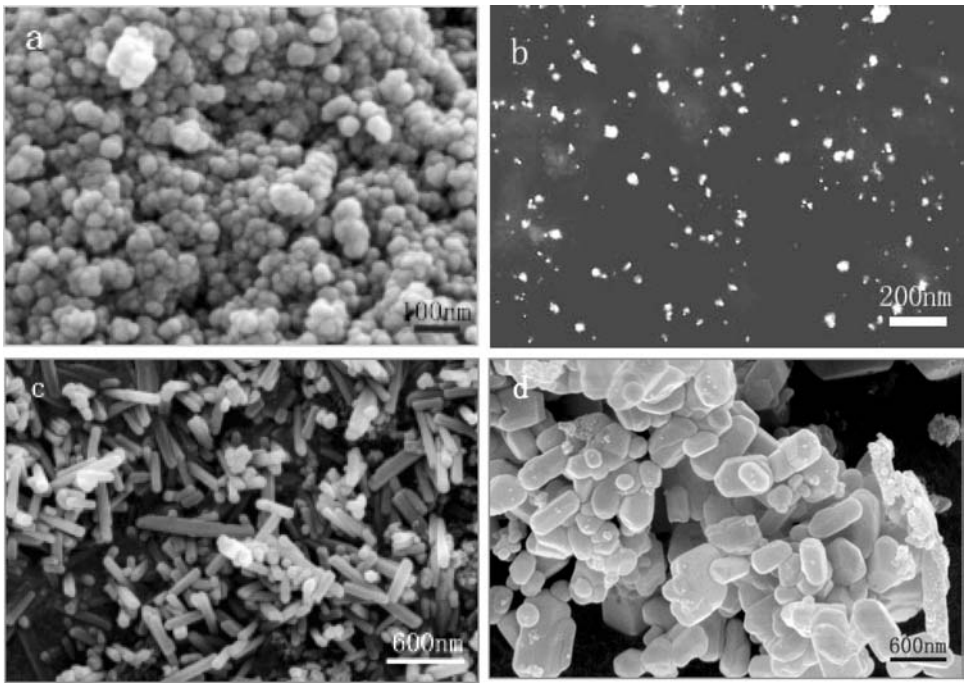

Figure 3 (a), (b) FE-SEM and TEM micrograph of prepared HAP nanoparticles by microwave interval heating (0.5 min); (c) typical FE-SEM micrograph of the HAP nanorods by microwave interval heating for (1 min); (d) FE-SEM micrograph of the prepared HAP aggregations with continuous microwave heating (1 min).

conventional heating at as low temperature as 80 °C for 6 hr. However, in our microwave-heating experiments, the PO_4^{3-} ions possess strong polarizability and thus are excellent microwave-absorbing agents that can heat the reagents to the desired temperature in very short time. It has been reported [17, 18] that when salt with crystalline water reacted with other reactants, the crystalline water within it was considered to be released from the structure of its molecules forming a layer of liquid film over particles, which in fact constructed a micro-aqueous-environment for the reactant molecules. So the crystalline water of reagent can greatly reduce solid-state reaction temperature and accelerate the reaction rate. So the microwave heating together with crystalline water of the reagents facilitates the diffusion of reagents, nucleation and growth of HAP products. The easily accessible HAP in the form of rods instead of particles under proper microwave heating condition is explained as follows: hexagonal HAP has an intrinsic (0 0 2) preference growth face, which facilitate the formation of rods rather than particles; besides, the movement and polarization of PO_4^{3-} under the rapidly changing electric field of the microwave result in transient, anisotropic microdomains for the reaction system, facilitating the anisotropic growth of nanorods structure.

In summary, HAP nanorods with diameters from 60 to 80 nm and lengths of about 400 nm have been successfully prepared by a simple one-step microwave-assisted solid-state reaction at room temperature. We also compared microwave heating with conventional heating in the synthesis of HAP and investigated the effects of microwave heating time on the morphology of the products. We preliminarily concluded that microwave radiation plays an important role in the synthesis of HAP nanorods, because it can lead to much shorter reaction time and easier work-up. Hence, it is a breakthrough over classical synthesis methods.

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