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Synthesis of hydroxyapatite nanorods from abalone shells via hydrothermal solid-state conversion

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ABSTRACT

Hydroxyapatite (HAP) has been widely applied as a biomaterial for repairing or substituting human hard tissues. In this paper, HAP nanorods were successfully produced from abalone shell powders via hydrothermal solid-state conversion without surfactants or complex agents. The field emission scanning electron microscopy (FESEM) showed that the produced HAP exhibited the typical rod-like structure. Based on the X-ray diffraction (XRD) and thermal analysis (thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)), these samples contain a small amount of aragonite and calcite crystals, and their content gradually decreases by prolonging the hydrothermal time. However, this decrease only slightly changes for the longer times. The Fourier transform infrared spectroscopy (FTIR) revealed that organic matter was detected in the samples without adding surfactants or complex agents. This study provides a solution to the resource waste and environmental pollution caused by abandoned abalone shells, and we also synthesized HAP for potential bone repair materials.

1. Introduction

As a type of marine mollusk, abalone (Haliotis) is a typical single shell shellfish. Because of its delicious taste and high nutrition values, abalone meat is a rare ingredient of traditional Chinese food and one of the necessary dishes for Chinese banquets. However, the abalone shell is a great burden to the environment after consumption of the abalone meat. Thousands of tons of shells were found abandoned on an island and around a town (shown in Fig. 1). This not only resulted in waste of natural resources, but also polluted the environment. Abalone shell is a natural composite material. It is composed of more than 95 wt.% calcium carbonate [1,2] and less than 5 wt.% organic matter [3–5]. Thus, abalone shell is a good source of calcium. Until now, there have been few reports on the efficient use of abalone shells.

Hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) is the most stable form of calcium phosphate and is slightly soluble in water [6–8]. It is the main inorganic component of mammalian hard tissues, such as bones and teeth [9,10]. The HAP content of human enamel is about 96 wt.%. Generally, synthetic biomaterials have excellent bioactivity, biocompatibility and osteoconductivity [11–14]. For this reason, synthetic nano-HAP has been widely applied as a biomaterial for repairing or substituting human hard tissues [15–17]. In recent years, methods to prepare nano-HAP using different forms of the raw material have been reported, including solid-phase synthesis [12,18], sol–gel method [19,20], template synthesis [12,21,22], and the hydrothermal method [12,23–25], among others. However, the solid-phase synthesis method requires processing with high temperature. Template synthesis is necessary to add organic templates; however, it is not easy to degrade after implanting into the organism, which limits the clinical applications. Fortunately, the hydrothermal synthesis method can make use of the original mineral that is poorly soluble or insoluble. Additionally, ion exchange and recrystallization occur, which make a smooth solid-state conversion from one mineral phase to another realizable under hydrothermal conditions. Moreover, solid-state conversion reduces the calcination and milling steps. Hence, it is easy to control the reaction conditions. Thus far, some scholars have reported the synthesis of HAP using calcium carbonate with different forms [24,26], but it is still a challenge to synthesize well-organized nano-HAP with an expected composition and mechanical properties using abalone shell powders under hydrothermal conditions.

Herein, we utilized abalone shell powders as a calcium source for HAP. HAP nanorods were successfully synthesized via hydrothermal solid-state conversion. The crystal phase and morphology of the samples were characterized using X-ray diffraction (XRD), field emission

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Fig. 1. Abandoned abalone shells.

scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), zeta potential measurements (ZP) and a thermo gravimetric analyzer.

2. Materials and methods

2.1. Materials

The shells of Wrinkles Abalone were collected from the official dock Ocean Development Co., Ltd (Lianjiang Country in Fujian Province, CN). Diammonium phosphate ($(NH_4)_2HPO_4$, ≥99%) was purchased from Sinophar Chemical Reagent Co., Ltd, China. Sodium hydroxide (NaOH, 98%) and acetic acid (CH_3COOH, ≥99.5%) were purchased from Shanghai Lianshi Chemical Co., Ltd (Shanghai, CN).

2.2. Preparation of the samples

First, the abalone shell was immersed in 10 vol.% acetic acid solution to clean off the surface impurities. After rinsing with distilled water and naturally dying them, the abalone shell was crushed and screened using a pulverizer (SF-130, Zhong Cheng Pharmaceutical Machinery Factory, CN). This produced the abalone shell powders.

For the synthesis, abalone shell powders and diammonium phosphate ($(NH_4)_2HPO_4$) were used as the calcium and phosphorous sources, respectively. The samples were prepared as follows: 2 g of abalone shell powders and 1.5847 g of $(NH_4)_2HPO_4$ were mixed (Ca/P in a molar ratio of 1.67:1), and they were dissolved in 20 ml of deionized water. The pH of the solution was adjusted to 10 using sodium hydroxide solution (NaOH, 1 M) and the mixture was stirred at room temperature for 30 min using a magnetic stirrer. Then, the mixed solution was transferred to an autoclave, and heated at 150 °C at hydrothermal times of 6 h, 18 h, and 72 h. After completing the reaction, the final precipitate was washed with deionized water via centrifugation several times. Finally, the white latex-like precipitant was freeze-dried to yield white powders. This produced the samples.

2.3. Characterization of the samples

The phase of the samples was examined using X-ray diffraction (XRD, X'Pert PRO Panalytical diffractometer) with Cu Kα (λ = 0.154056 nm) incident radiation at a working voltage of 40 keV in the range of 10° to 70° at a 0.02° step size. The phases were identified by comparing the data with data reported in the Joint Committee of Powder Diffraction Standards database (JCPDS no. 09-0432).

For FTIR, (Nicolet 360 intelligent spectrometer, Thermo Nicolet Corporation, US) studies, we used the KBr pellet method, which was performed on dried samples.

The microstructure and surface potential of the sample were analyzed using FESEM, (Nova NanoSEM, FEI, Netherlands) and a potential instrument (Malvern Zetasizer Nano-ZS90).

A thermogravimetric analyzer (TGA, DIL402C, NETZSCH, Germany) further determined the composition of the obtained HAP. The samples were heated to 1000 °C in flowing air at a heating rate of 10 °C/min.

3. Results and discussion

Fig. 2 shows the XRD patterns of the abalone shell powders (A) and the samples exposed to different hydrothermal times of (B) 6 h, (C) 18 h, and (D) 72 h. In Fig. 2A, the abalone shell was determined to be composed of aragonite and calcite. After the hydrothermal treatment, most of the diffraction peaks of the calcium carbonate (aragonite and calcite) disappeared, whereas the HAP phase diffraction peaks were detected at 2θ of 25.77°, 31.81°, 32.12°, 34.01°, 39.97°, 46.74°, and 49.38°. Moreover, the intensity of the diffraction peaks is increased as a function of the prolonged hydrothermal treatment time at 2θ of 25.77°, and 31.81° (shown in Fig. 2D). This suggested that the crystallinity of the samples also increased. Moreover, the weak diffraction peaks of the calcite and aragonite (at the 2θ of 29.38° and 33.08°, respectively) were observed even after hydrothermal treatment for 72 h. This may be due to the natural structure and special composition of the abalone shell [1,27,28].

To further investigate the composition of the samples exposed to different hydrothermal times of (B) 6 h, (C) 18 h, and (D) 72 h, FTIR analysis was conducted (Fig. 3). The bands at 1789 cm^{-1}, 1464 cm^{-1}, 862 cm^{-1} and 710 cm^{-1} represent CO_3^{2-} (shown in Fig. 3A), which is due to the composition of the abalone shell that contains calcium carbonate (aragonite and calcite). After the hydrothermal treatment, the components of all the samples were similar, which showed the presence of the characteristic groups of the HAP. The characteristic vibration of the PO_4^{3-} groups was detected at 1037 cm^{-1}, 960 cm^{-1}, 608 cm^{-1} and 567 cm^{-1}. The band at 3567 cm^{-1} was assigned to the stretching vibration of the OH^-. Additionally, the vibration peaks at 1462 cm^{-1}, 1418 cm^{-1}, and 874 cm^{-1} represent CO_3^{2-}. These bands are due to calcium carbonate entrapped inside the HAP, which is consistent with the XRD results. C—H asymmetric stretching vibration and symmetric stretching vibration were detected at 2929 cm^{-1} and 2856 cm^{-1}, respectively. These bands demonstrated that organic matter exists in the synthesized HAP. This particular organic matter originates from the

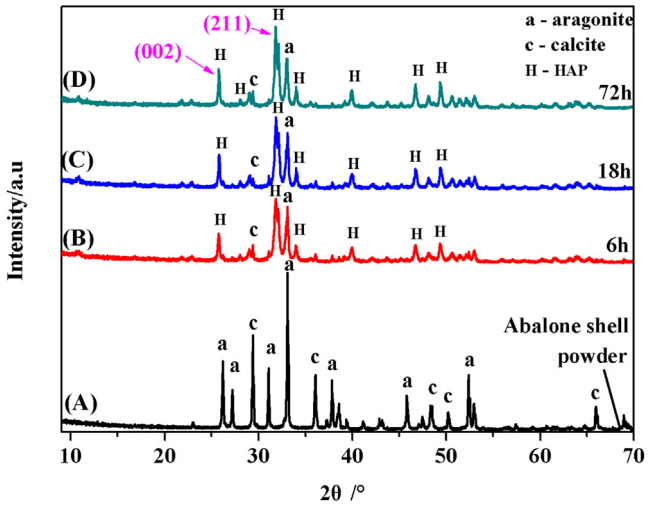

Fig. 2. XRD patterns of the abalone shell powders (A) and the samples exposed to different hydrothermal times: (B) 6 h, (C) 18 h, and (D) 72 h.