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Effects of heat treatment on the synthesis of hydroxyapatite from eggshell powders

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Abstract

Daily, several million tons of eggshells are being generated as biowaste around the globe. The wide availability and natural-biological origin of the eggshells, containing several trace elements that will remain in the crystalline structure of synthesized hydroxyapatite (HA), make their composition similar to human bone. These advantages will benefit the overall physiological functioning after implantation. In this study, we propose a cost-effective and straight-forward technique for converting calcium carbonate obtained from eggshells into highly pure and crystalline HA via ball milling and subsequent heat treatment. Detailed analysis of the prepared samples confirm the formation of high phase-purity HA by milling dicalcium phosphate dihydrate (DCPD) and eggshell powders for 1 h followed by sintering at 1200 °C for 1 h. Besides, samples composed of biphasic calcium phosphate (HA + β-TCP) can easily be prepared by varying the heating temperature and time. The carbonate peaks observed in the Fourier transform infrared spectrum of the as-received HA powder can be associated with the A- and B-type carbonated structure.

Keywords: Eggshell; Hydroxyapatite; β-tricalcium phosphate; Heat treatment

1. Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA), one of the major mineral constituents of vertebrate bone and tooth, is the most well-known crystalline phase of calcium phosphate (CaP) [1]. In general, HA is used for repairing bone defects and bone augmentation due to its superior biocompatibility, osteoconductivity, and bioactivity [2]. Besides, all apatite minerals show good properties as ion exchangers. Given this advantage, HA-based materials are also used for the removal of heavy metals in wastewater and soil treatment, amongst others [3]. Therefore, several studies have reported the preparation of HA. In general, HA is prepared using two main approaches, namely, the wet method and the solid-state reaction. The wet method can be further classified as aqueous precipitation, hydrothermal techniques, and the hydrolysis of other calcium phosphates [4–7]. However, the wet chemical synthesis methodologies are rather time consuming, complicated and demand adept adjustment and control of the pH value. Given these shortcomings of the wet synthesis methods, the dry process is considered to be more suitable for the large-scale synthesis of high crystalline HA because of its high reproducibility and low processing cost [8,9].

Typically, majority of HA and other calcium phosphates are produced by chemical synthesis using several different methods. However, these materials can also be produced from natural by-products or wastes. These biological compounds are generally denoted as calcium-deficient, containing a wide variety of relative small amounts of other substitute atoms or groups such as carbonate ions. HA can incorporate a wide variety of substitutions for Ca^{2+}, PO_4^{3-}, and/or OH^- ions

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[10]. A recent study has reported the production of HA from bovine bones using a subcritical water process and alkaline hydrothermal hydrolysis [11]. According to the study reported by Piccirillo et al. [12], calcium phosphate biphasic material consisting of HA and β-tricalcium phosphate (β-TCP) could be prepared by simple annealing of the bones of salt codfish, a by-product from the food industry. Roy and Linnehan in 1974 were the first to propose the hydrothermal transformation of corals into HA [13]. Besides, Hu et al. [14] studied the hydrothermal conversion of Australian corals into HA. However, corals are not available worldwide and some coral species are in danger of extinction. Therefore, it is highly imperative to identify alternative materials that are renewable, cost-effective, and also easily accessible.

Eggs are used in huge quantities in food processing, baking and hatching industries. After utilizing the egg contents, the eggshells are generally discarded. The eggshells thus generated favor microbial growth and lead to environmental pollution. However, the eggshells, which are readily available from wastes, present a promising future since it can be used as a precursor material for the synthesis of HA. Besides, using a biological-substituted apatite containing several trace elements that will remain in the crystalline structure of synthesized HA will make its composition resemble human bone, thereby benefiting the overall physiological functioning after implantation [15]. The aim of the present work is to propose a cheap method for the synthesis of HA powder or biphasic calcium phosphates through solid-state reaction using dicalcium phosphate dihydrate ($CaHPO_4 \cdot 2H_2O$, DCPD) and eggshell powders as the starting material. In the typical process, the two precursor powders were initially mixed using ball milling and heat-treated at various temperatures for various time durations. The as-synthesized materials were characterized using X-ray diffraction, Fourier transform infrared spectroscopy, and scanning electron microscopy.

2. Materials and methods

In this study, DCPD (Yakuri Chemicals Co., Ltd., Japan) and eggshell powders were used as starting materials. Raw membrane-bound hen eggshell samples were collected from a breakfast shop in the university campus and immediately stored in a refrigerator. The eggshells were pretreated by stripping the membrane off the eggshell, rinsing with water, drying, and then crushing and powdering using an agate mortar. The eggshell powders thus obtained were sieved using a 325-mesh sieve. Subsequently, the hand-ground eggshell powders and DCPD were homogeneously mixed with deionized water in a zirconia container. The ratio of eggshell powders to DCPD was 4:3 (mole ratio). The resulting mixture was wet-milled in a planetary ball-milling machine (QM-3SP4J, Nangjing, China) for 1 h at a speed of 170 rpm in a zirconia bottle. After milling, the slurry was dried completely in a convection oven at 150 °C for 24 h. Following that, the dried powder was heat-treated at a rate of 10 °C/min and maintained at various temperatures (900, 1000, 1100, or 1200 °C) for various durations (1, 3, 5, or 10 h) in several independent experiments.

The crystalline phases of the powders after heat treatment were analyzed by using powder X-ray diffraction with Cu Kα radiation (XRD; XRD-6000, Shimadzu, Japan). The phases were identified by comparing the experimental X-ray diffractograms with the standards compiled by the Joint Committee on Powder Diffraction Standards (JCPDS). The microstructure of the powders was observed using a scanning electron microscope (SEM; JSM-6700 F, JEOL, Japan) under secondary electron mode. Furthermore, the Fourier transform infrared (FTIR; Bio-Rad, FTS-40, USA) spectra of the powdered samples were obtained in the wavenumber range of 600–4000 cm^{-1}.

From the XRD data, the absolute values of crystallinity (X_c) of the HA particles were calculated according to the following equation [16]:

$$X_c = 1 - \frac{V_{112/300}}{I_{300}},$$

where I_{300} is the intensity of (300) diffraction peak and $V_{112/300}$ is the intensity of the hollow between (112) and (300) diffraction peaks of HA.

The average crystallite size of the synthesized HA particles was calculated by using the Scherrer's formula as follows [17]:

$$X_s = \frac{0.9\lambda}{\mathrm{FWHM}\cos\theta},$$

where X_s is the average crystallite size (nm); λ is the wavelength of the X-ray used for the analysis (1.5406 Å); FWHM is the full width at half maximum for the diffraction peak under consideration (rad); and θ (degree) is the Bragg angle. In this study, the (002) diffraction peak was chosen for calculation of the crystallite size since it was isolated and sharper than the others.

3. Results and discussion

3.1. Effects of heat treatment temperature

Fig. 1 shows the XRD patterns of the samples synthesized by milling DCPD and eggshell powders for 1 h and then heat-treated at different temperatures (900, 1000, 1100, and 1200 °C) for 1 h. The results show that the heat treatment temperature plays an important role in the formation of HA. Upon heat treatment at 900, 1000, and 1100 °C for 1 h, the diffraction peaks corresponding to unreacted $Ca_2P_2O_7$ (pyrophosphate derived by the heat treatment of DCPD) and CaO (obtained by the heat treatment of eggshell powders) are still observed in the samples. However, the intensities of these precursors gradually decrease with an increase in the treatment temperature and completely disappear with an increase in heating temperature to 1200 °C. This indicates that the unreacted precursors have been incorporated into the HA and β-TCP lattice through high temperature diffusion. It is evident from Fig. 1 that the formation of HA phase is initiated by sintering the milled sample at 900 °C for 1 h and that the