

# Synthesis of hydroxyapatite from eggshell powders through ball milling and heat treatment



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## ABSTRACT

Every day, several million tons of eggshells are being generated as bio-waste across the world. This study demonstrates the synthesis of HA powder using dicalcium phosphate dehydrate (CaHPO<sub>4</sub>·2H<sub>2</sub>O, DCPD) and eggshell powders via ball milling and subsequent heat treatment. The formation of HA phase can be initiated by sintering the 1 h milled sample at 1000 °C for 1 h, while pure HA phase can be obtained upon sintering the 10 h milled sample. Additionally, the final products composed of biphasic calcium phosphate (HA + β-TCP crystals) can easily be prepared by ball milling for 5 h followed by heat treatment at 1000 °C for 1 h. The carbonate peaks observed in the FTIR analysis of the as-prepared HA closely matched those of A- and B-type carbonates, which is typical of the biological apatite. The elemental composition of the as-synthesized HA showed the presence of Ca, P, Mg, and Sr.

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## 1. Introduction

Hydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>, HA) is being actively investigated as a potential catalyst or a catalyst support for a variety of chemical reactions [1,2]. Besides, HA is also being analyzed as an adsorbent for environmental protection, owing to its strong affinity toward heavy metal ions [3,4]. Furthermore, synthetic HA finds application in various medical and dental applications as a promising material for healing damaged bones and teeth, for implant and scaffold, and as a drug delivery agent, due to its biocompatibility and bioactivity as well as its similarity to the inorganic component of the hard tissues in natural bones [5,6]. However, the properties of natural apatite crystals and conventional synthetic stoichiometric HA are significantly different [7]. For example, the natural apatite in the human body contains significant amounts of carbonate and trace elements [8,9]. Natural bone is clearly a non-stoichiometric HA [10]. The properties of synthetic HA are largely determined by its particle size, morphology, crystallinity, and composition, which in

turn depend on the synthesis precursors and processing conditions [11].

To this end, a variety of synthesis techniques, including sol-gel [12], aqueous precipitation [13], hydrothermal technique [14–16], and solid-state reactions [17–19] have been reported for the synthesis of HA. Over the past years, biologically derived natural materials, such as fish bone, bovine bone, corals, oyster shell, and eggshells, have been converted into useful biomaterials like HA. For instance, the study reported by Lemos et al. [20] demonstrates the transformation of natural aragonite from cuttlefish bone into HA via hydrothermal treatment at 200 °C. Ooi et al. [21] reported the synthesis of porous HA from bovine bone via heat treatment in the temperature range of 400–1200 °C. Sivakumar et al. [22] have demonstrated the conversion of coral into monophasic HA via a low temperature hydrothermal process. A recent study has demonstrated the synthesis of HA from oyster shell powders mixed with calcium pyrophosphate (Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub>) or dicalcium phosphate dehydrate (CaHPO<sub>4</sub>·2H<sub>2</sub>O, DCPD) by ball milling and subsequently heat treatment [18]. More recently, Ho et al. [16] synthesized nanosized HA via hydrothermal treatment of eggshell and several biomolecules obtained from waste materials (pomelo, grape, and sweet potato peel extracts). These materials offer promising opportunities, given the fact that the raw materials are wastes. Besides, the use of ‘biological apatite’ containing some trace elements as bone substitutes, instead of ‘chemical apatite’, would be much beneficial for bone defect healing [23].

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Eggshells generated after breaking eggs represent a significant waste because they become typically useless after the use of egg contents and its derivatives. Such eggshell wastes are commonly disposed of in landfills without any pre-treatment. Such activities are highly undesirable to the environment, especially from the viewpoint of the odor generated during the biodegradation. Eggshells constitute 11% of the total weight of the egg and are mainly composed of calcium carbonate ( $\text{CaCO}_3$ ) [24]. In the present investigation, an attempt has been made to synthesize pure and bone-like HA powder from eggshells. The eggshell powder, which was used as the Ca source, was combined with DCPD powder. In the typical process, the powder mixture was ball-milled for 1, 5, and 10 h, followed by heat treatment at  $1000^\circ\text{C}$  for 1 h. Although there are several reports on the synthesis of HA from eggshells, most processes are done by wet chemical methods. Clearly, this technique is lengthy, complicated and require pH adjustment and control. To the best of our knowledge, no study has reported the synthesis of HA powder using DCPD and eggshell powders via ball milling and subsequent heat treatment. This study shows a great potential for the conversion of eggshell waste into highly valuable compounds using simple yet effective processes.

## 2. Materials and methods

In this study, DCPD (Yakuri Chemicals Co., Ltd., Japan) and eggshell powders were used as starting materials for the synthesis of HA. Raw membrane-bound hen eggshell was collected from a breakfast shop in the university campus and immediately stored in a refrigerator. The eggshells were pre-treated by stripping the membrane off the eggshell, followed by 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 powder 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, Nanjing, China) for 1, 5, or 10 h at a speed of 170 rpm in a zirconia bottle. After milling, the slurry was dried completely in a convection oven at  $150^\circ\text{C}$  for 24 h. Following that, the dried powder was heated to  $1000^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ , and subsequently held at that temperature for 1 h.

The crystalline phases of the ball-milled powders before and after heat treatment were analyzed by using powder X-ray diffraction with Cu  $K\alpha$  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 scanning electron microscope (SEM; JSM-6700F, 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  $600\text{--}4000\text{ cm}^{-1}$ . The composition of the synthesized powders was analyzed by using inductively coupled plasma-atomic emission spectroscopy (ICP-AES; ICAP 9000, Jarrell-Ash Co., USA).

From the XRD data, the crystallinity ( $X_c$ ) of the HA particles was calculated according to the following equation [25]:

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

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.

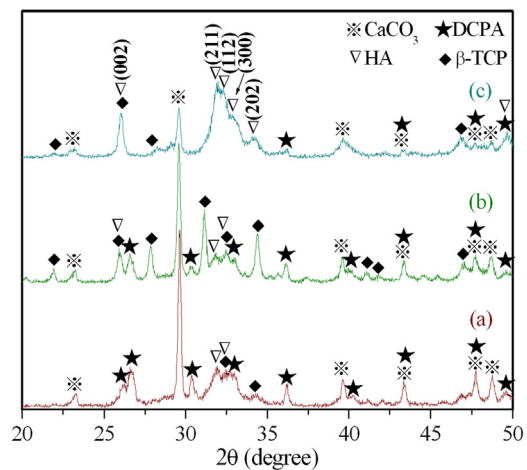


Fig. 1. XRD patterns of the powders produced by milling DCPD and eggshell powders for various durations (a) 1, (b) 5, and (c) 10 h.

The average crystallite size of the synthesized HA particles was calculated by using the Scherrer's formula as follows [26]:

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

where  $X_s$  is the average crystallite size (nm);  $\lambda$  is the wavelength of the X-ray used for the analysis ( $1.5406\text{ \AA}$ ); FWHM is the full width at half maximum for the diffraction peak under consideration (rad) and  $\theta$  ( $^\circ$ ) is Bragg's angle. In this study, the (002) diffraction peak was chosen for calculation of the crystallite size since it was isolated and sharper than the other peaks.

## 3. Results and discussion

### 3.1. Characterization of ball-milled powders

Fig. 1 shows the XRD patterns of the DCPD and eggshell powder mixtures milled for 1, 5, and 10 h. As can be seen from the diffraction pattern of the 1 h milled powder, the peaks mainly correspond to dicalcium phosphate anhydrous (DCPA) and  $\text{CaCO}_3$  with trace amounts of  $\beta$ -TCP and HA phase. The DCPD precursor completely decomposed to DCPA because of the increased temperature and vigorous stirring during ball milling [27]. Upon milling for 5 h, the intensities of DCPA and  $\text{CaCO}_3$  decreased with the obvious appearance of diffraction peaks corresponding to  $\beta$ -TCP phase, together with trace amounts of HA phase. With further increase in milling time to 10 h, the diffraction peaks indicated the formation of HA phase with small amounts of DCPA and  $\text{CaCO}_3$  from precursors. When compared to 5 h milled sample, the XRD pattern of the 10 h milled sample shows a decrease in  $\beta$ -TCP content, which indicates the gradual replacement of  $\beta$ -TCP by HA.

The microstructure of the DCPD and eggshell powders milled for 1, 5, and 10 h showed remarkable differences in size and shape (Fig. 2). The reduction in the particle size was greater with increase in milling time. The microstructure of the powders milled for 1 and 5 h showed larger particles of irregular shape and non-uniform size distribution, which could be related to the unreacted precursors. The submicron-sized particles observed in the 5 h milled sample could possibly be related to the  $\beta$ -TCP and HA phase. However, with increase in milling time to 10 h, the microstructure revealed smaller particles with relatively uniform size distribution.

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