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Original Research Paper

Preparation and characterization of hydroxyapatite synthesized from oyster shell powders

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ABSTRACT

The ready availability and the low cost of oyster shells, which is composed predominantly of calcium carbonate with rare impurities, along with natural wastes are attractive features for converting the biological material into hydroxyapatite (HA) powders for biomedical applications. The HA powder was synthesized using oyster shell powders and dicalcium phosphate dihydrate ($CaHPO_4{\cdot}2H_2O$, DCPD) through ball milling and subsequently heat treatment. The HA was initiated through sintering the 1-h milled sample at 1000 °C for 1 h, while pure HA phase is formed after sintering the 10-h milled sample. The as-prepared samples, obtained after 5 or 10 h of milling and then heat-treating at 1000 °C for 1 h, contain the phase of β-tricalcium phosphate (β-TCP). Moreover, the result of FTIR analysis showed that the as-prepared HA sample is A- and B-type carbonate-containing calcium phosphates. The as-synthesize HA powder containing trace elements Mg and Sr exhibited good crystallinity (96.3%) and high phase-purity.

1. Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA) is the main inorganic calcium phosphate mineral component of human bones and teeth. It has been used extensively for many clinical applications due to its excellent biocompatibility, and good bioactivity and osteoconductivity [1,2]. Much effort has been placed on the synthesis of HA samples via different methods, such as wet chemical methods [3], hydrothermal processes [4], sol-gel synthesis [3], and solid-state reaction [5]. The wet process technique is lengthy, complicated and require pH adjustment and control. Therefore, when preparing highly crystalline powders for large-scale production, the dry process is a more suitable way because it shows high reproducibility and low processing cost [6].

Most of the main Ca sources used in preparing HA were chemical agents through wet or dry process. Recently, a number of synthesis techniques have been widely developed using bio Ca like fish bone, bovine bone, corals, eggshells, oyster shells, etc. Rocha et al. [7] obtained the transformation of natural aragonite from cuttle-fish bone into HA by hydrothermal method. Also, Barakat et al. [8] extracted HA from bovine bone using a subcritical water process and alkaline hydrothermal hydrolysis. Xu et al. [9] prepared porous coralline hydroxyapatite by a hydrothermal conversion of marine coral Porites skeleton. Ho et al. [5] proposed a method of producing calcium phosphate bioceramics from eggshell waste; they also synthesized nanosized HA through a hydrothermal method by using eggshell and fruit peel waste extracts [4]. Wu et al. [10] fabricated pure HA or HA + β-tricalcium phosphate (β-TCP) through ball milling and subsequently heat treatment using oyster shell powders and calcium pyrophosphate ($Ca_2P_2O_7$) or dicalcium phosphate dihydrate ($CaHPO_4{\cdot}2H_2O$, DCPD). Recently, Chinese mystery snail shells were recycled as a Ca source to prepare HA under hydrothermal processing [11].

Oyster shells are biological wastes, which is mainly composed of $CaCO_3$ (96%) and minor amounts of other minerals. Biological apatites attract special attention due to the substitutions at the OH^-, Ca^{2+}, and PO_4^{3-} sites of HA and the presence of several trace elements can enhance the overall biological performance of the biomaterial [12,13]. In the present investigation, a simple process was developed to prepare HA powders or biphasic calcium phosphates through planetary ball milling followed by heat treatment. The oyster shell powders were used as the Ca source to be combined with dicalcium phosphate dihydrate. Powder mixture was

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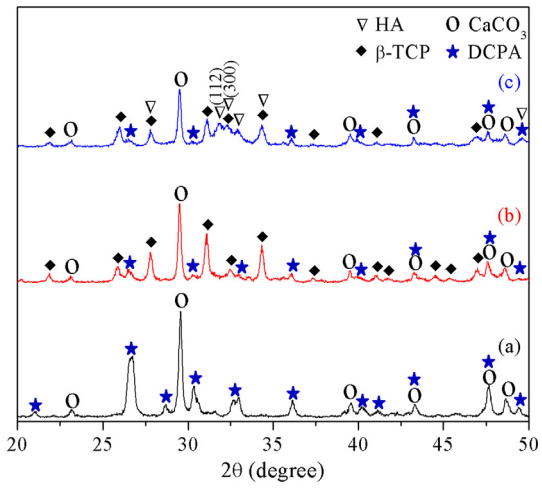

Fig. 1. XRD patterns of the products synthesized from DCPD and oyster shell powders milled for various durations. (a) 1, (b) 5, and (c) 10 h.

ball milled for 1, 5, and 10 h durations before heat treatment at 1000 °C for 1 h. In this study, we present a great potential for the conversion of this oyster shell waste into highly valuable bioceramics, using simple and effective approaches.

2. Materials and methods

Specimens of the *Crassostrea gigas* were collected from Wanggong beach, Taiwan. The oyster shell powders and DCPD (Yakuri Chemicals Co., Ltd., Japan) with given stoichiometric proportionality (Ca/P = 1.67) were homogeneously mixed with deionized water in a zirconia container. They were then put into a planetary ball milling machine (QM-3SP4J, Nangjing, China) in wet milling for 1, 5, or 10 h under air atmosphere. Subsequently, the milled slurries were dried in a convection oven at 150 °C for 24 h. These powders were then heated to 1000 °C for 1 h.

The phase analyses of the powders before and after heat treatment were carried out by powder X-ray diffraction (XRD; XRD-6000, Shimadzu, Japan). Powder morphology and particle size were evaluated using a scanning electron microscope (SEM; JSM-6700F, JEOL, Japan). The chemical composition of products was performed using energy-dispersive X-ray spectroscopy (EDS) coupled with the SEM. Fourier transform infrared (FTIR; Bio-Rad, FTS-40, USA) spectroscopy was applied to the study of functional groups present in the powdered samples. The weight loss and thermal stability of the synthesized powders were also studied to determine the phase transition temperature using differential thermal analysis (DTA; Q600 SDT, TA Inc., US) from room temperature to 1400 °C at a heating rate of 5 °C/min. From the XRD data, the crystallinity (X_c) of the HA particles was calculated according to the fraction of crystalline phase present in the examined volume [14]. The crystallite sizes of the synthesized powders were determined from Scherrer's formula [15].

3. Results and discussion

3.1. Characterization of ball-milled powders

Fig. 1 shows XRD patterns of DCPD and oyster shell powder mixtures milled for different durations. After 1 h of grinding, the principal diffraction lines correspond to dicalcium phosphate anhydrous (DCPA) and $CaCO_3$. DCPD completely decomposed to DCPA after ball milling, because increased temperature and vigorous stirring both forced the DCPD to transform into DCPA [16]. After 5 h of milling, the intensities of DCPA and $CaCO_3$ decreased and the obvious diffraction peaks of β-TCP phase appeared. With increasing milling time up to 10 h, HA phase was prepared with small amounts of DCPA and $CaCO_3$ from precursors. The content of β-TCP decreases with the increasing ball-milling time from 5 to 10 h, which indicated a gradual replacement of β-TCP by HA.

Fig. 2 shows the microstructure of the DCPD and oyster shell powders milled for 1, 5, and 10 h, indicating remarkable differences in size and shape. With an increase in milling time, the particle size reduces gradually. The powders milled for 1 and 5 h were

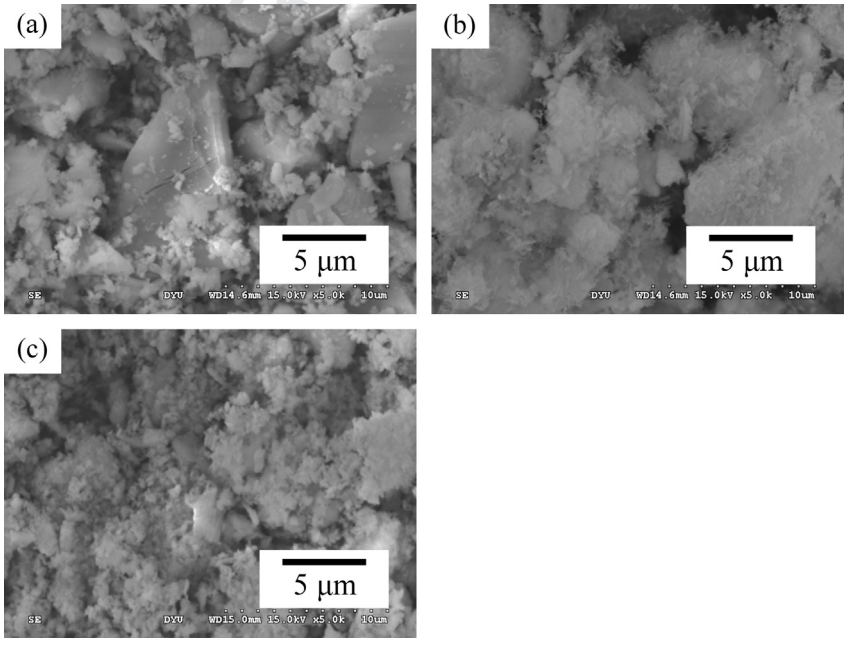

Fig. 2. SEM images of DCPD mixed with oyster shell powders milled for various durations. (a) 1, (b) 5, and (c) 10 h.

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