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Characterization and annealing performance of calcium phosphate nanoparticles synthesized by co-precipitation method

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Abstract

Calcium phosphate ceramics (CPCs) nanopowders were synthesized via co-precipitation microwave technique. The influence of pH value and annealing temperature on the crystallinity, particle shape, morphology, surface area and microhardness was investigated. The results showed that the pH value is the crucial factor in the phase decomposition. The aspect ratio of the particles was found to decrease with increasing pH. In addition, the microhardness values were improved with the increase of pH value that was linked directly to the enhancement of the crystallinity.

Keywords: Calcium phosphate ceramics; Hydroxyapatite; HRTEM; FESEM

1. Introduction

Bioceramics are designed to relieve the pain and recondition the functions of diseased or damaged hard tissues (bones and teeth) of the body [1]. Calcium phosphate ceramics (CPCs) resemble to the mineral composition of human hard tissues [2]. In addition to being non-toxic and an adequate biodegradation rate, they have excellent biocompatibility and good osteoconductivity [3–5]. Therefore, calcium phosphate-based biomaterials and bioceramics are now used in a number of different applications such as dental implants and a substitution of bony and periodontal defects [6], tissue engineering systems [7], bone regeneration, orthopedics, middle ear implants [8] and bioactive coating on metallic implants [9]. Their suitable biodegradable rate makes them a good drug delivery vehicle [10–13]. Moreover, they have been used in non-medical fields, like gas sensors, and heavy metals removal [14]. Even so, the main limitations to use CPCs for load bearing are their poor mechanical properties; especially, they are brittle and have a poor fatigue resistance [15–17]. This forementioned behavior results from the porosity [17]. On the other hand, the porosity is thought to enhance the biodegradability and bioactivity by increasing the surface area available for reaction [18].

The nano-CPCs were previously prepared using chemical methods such as: precipitation [19], sol–gel [20], microemulsion method [21], hydrothermal treatment [22,23], etc. Each method has its own advantages and disadvantages. Among the most used methods, the co-precipitation one is the simplest with low cost; it can produce bone like structure [24]. The disadvantages of the co-precipitation included the low crystallinity products with the agglomerated particles [25].

One can overcome the agglomeration of the articles by using organic dispersants like EDTA [25]. In addition, the crystallinity could be improved using microwave and by annealing at high temperatures.

The aim of the present work is to manipulate the morphology of calcium phosphate nanoparticles by the variation in the preparation conditions such as pH value and annealing temperature. Another important goal is to better understand the relationship between microstructure and existing crystalline

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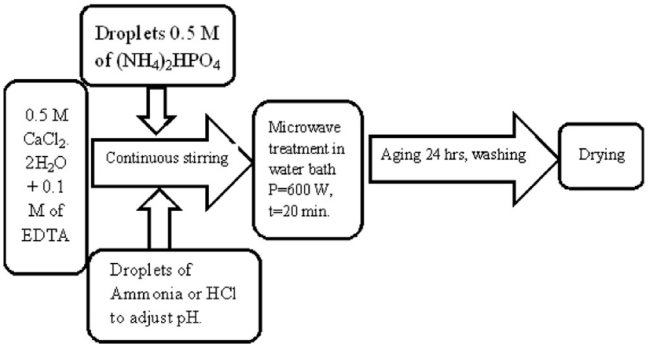

Fig. 1. Block diagram of calcium phosphate preparation by co-precipitation.

phases existing for complicated systems and how they could be exploited in enhancing the physico-chemical properties.

2. Materials and methods

Calcium chloride ($CaCl_2 \cdot 2H_2O$, Merck), diammonium phosphate ($(NH_4)_2HPO_4$, Merck) and EDTA were used as the starting materials. HCl (Merck) and NaOH (Merck) were used to control the pH of the solution mixture during the preparation procedure. 0.5 M of $CaCl_2 \cdot 2H_2O$ was dissolved with 0.1 M of EDTA in deionized water. $(NH_4)_2HPO_4$ was added drop wise to the calcium chloride solution with continuous stirring and the Ca/P ratio was adjusted at 1.67. Samples were prepared at pH values: 5, 6, 7, 9 and 11. The stirring was continued for several hours. The solution was kept in water bath into the microwave at 600 W for 20 min intermittent (to maintain the sample's temperature around 50–60 °C). The solutions were then aged for 24 h to precipitate. White precipitated powder was filtered and washed several times with double distilled water and finally dried at 50–60 °C for 12 h. The schematic diagram of preparation is shown in Fig. 1.

The obtained powders were pressed into pellets with 10 mm diameter using uniaxial press of 60 bar during 2 min. The pellets were annealed in Lenton furnace (UAF 16/5) at different annealing temperatures at; (800, 1000, 1100 and 1200 °C) for 2 h in air with a heating/cooling rate of 10 °C/min.

X-ray diffraction analyses were carried out using (analytical-x' pertpro with Cu $k_{\alpha 1}$ target, $\lambda = 1.5404$ Å, 45 kV, 40 mA, The Netherland) to identify the formation of the samples in pure single phase. FT-IR spectrometer (Perkin-Elmer system 2000) was used for recording FTIR spectra in the range of 4000–400 cm^{-1}. Thermo-gravimetry (TGA) analysis was carried out from room temperature up to 1200 °C in a DTG-60H SHIMADZU analyzer using an air flow rate of 100 ml/min and a heating rate of 10 °C/min. The atomic absorption data were carried out by (Perkin Elmer-AAnalyst 100-Germany). BET (Nova 2000 series – Quantachrome-USA) was used to get the surface area data. The surface morphology was studied suing field emission scanning electron microscope (FESEM) model QUANTAFEG 250 (The Netherlands). The EDX analysis was carried out by (EDX Genesis-The Netherlands). The particle size and shape were investigated by high-resolution transmission electron microscope (HRTEM) model JEOL/JME-2100. Microhardness

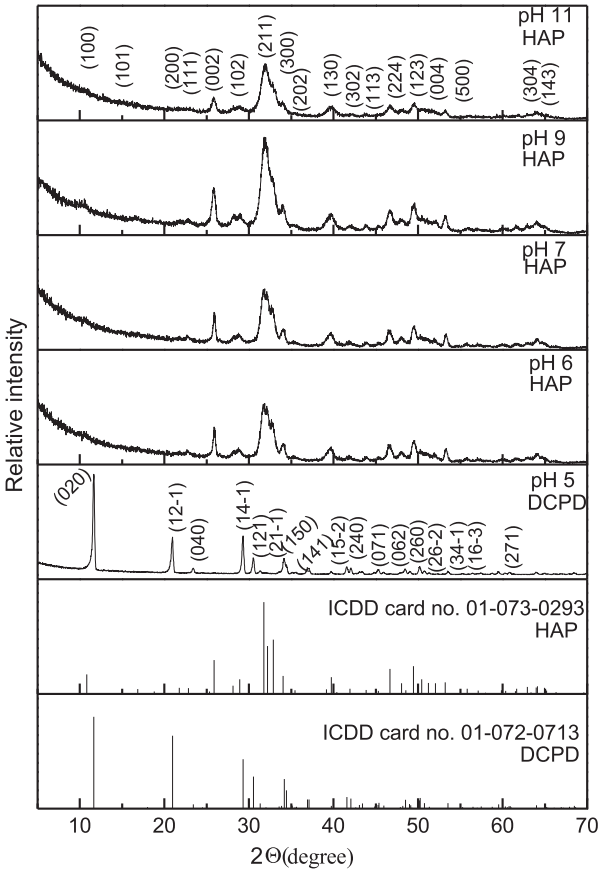

Fig. 2. XRD patterns of the as synthesized CPCs at different pH values.

experiments were carried out using (TTS UNLIMITED INC. model: HWDM-7/Japan) with situ imaging mode.

3. Results and discussion

Fig. 2 shows the X-ray diffraction (XRD) patterns for the synthesized powder using Ca/P molar ratio of 1.67. It is clear that the pattern of the powders with pH 5 revealed single phase of brushite with monoclinic symmetry space group (Ia) as compared and indexed with ICDD card no. 01-072-0713. When the pH value increased more than 5, it leads to the formation of hydroxyapatite in all samples in single phase with hexagonal symmetry ($P6_3/m$) as compared and indexed with ICDD card no. 01-073-0293.

The crystallite size of the synthesized powders was calculated using Scherrer formula ($L = 0.9\ \lambda/\beta\ \mathrm{Cos}\ \Theta$) where λ is the target wavelength, β is the corrected full width at half-maximum (FWHM) and Θ is the corresponding Bragg's angle [26].

It is clearly noted that the crystallinity of the samples was strongly dependent on the pH value. The calculated cell volume and crystallite size were reported in Table 1.

3.1. FTIR

Fig. 3 shows the FTIR spectra of obtained nanoparticles at different pH values for the as-prepared samples. In case of pH 5, the spectra exhibit easily recognizable bands as follows: the

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