



Effect of high-energy ball milling on the formation and microstructural features of carbonated chlorapatite nanopowders

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Received 29 October 2014; received in revised form 21 November 2014; accepted 4 December 2014

Available online 12 December 2014

Abstract

Carbonated chlorapatite nanopowders (n-CCAp) were synthesized by mechanochemical process from calcite (CaCO_3), phosphorus pentoxide (P_2O_5), and calcium chloride (CaCl_2) as raw materials. Results demonstrated that the formation of n-CCAp was influenced strongly by the milling time. At the beginning of milling (up to 15 min), CaCO_3 and CaCl_2 were the dominant phases, while P_2O_5 disappeared entirely due to its very high deliquescent nature. With increasing the milling time to 600 min, the progressive mechanochemical reaction was completed which resulted in the formation of nanostructured carbonated chlorapatite. According to the X-ray diffraction data, crystallite size of the product decreased from 24 ± 1 to 21 ± 2 nm when the milling time increased from 180 to 600 min, respectively. Microscopic observations illustrated that the final product had a cluster-like structure which was composed of polygonal particles with an average particle size of approximately 15 ± 10 nm. To our knowledge, this is the first report of the production of pure n-CCAp; the synthesis reported here can be a promising candidate for use in biomedical applications. Structure and morphology evolution of product are reported here and have been studied by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM).

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Keywords: Carbonated chlorapatite; Milling time; Nanoparticles; Structural features; Microscopic observations

1. Introduction

The quality of life for many patients has been improved by the use of specially designed bioceramics for the repair of damaged parts of the body especially skeletal parts. Bioactive ceramics also have remarkable properties such as excellent biocompatibility, the ability to promote cellular functions, and osteoconductivity which impact on rapid bonding with living tissue [1,2]. Hydroxyapatite (HAp), fluorapatite (FAp) and chlorapatite (CAp) as well as carbonated apatite (CA) are the major forms of bioactive ceramics

which are employed in biomedical applications as potential bone-substitute materials [3]. These are formed by partial replacement of phosphate (PO_4^{3-}) or hydroxide (OH^-) groups by other species such as Cl^- , F^- , and CO_3^{2-} [4]. Among them, CA is the closest biomimetic solid resembling the minerals in calcified tissues which is typically 4–8 wt% in human body [3]. Recent studies showed that CA was more effective than pure HAp for skeletal implants due to its chemical and physical properties as well as its bone bonding capability [5]. This leads to a growing interest in the development of such substituted apatite materials.

Carbonated hydroxyapatite (CHAp), carbonated fluorapatite (CFAp), and carbonated chlorapatite (CCAp) are the typical forms of CAp in which carbonate ions (CO_3^{2-}) substitute in either hydroxide (OH^-), which is known as type A ($\text{Ca}_{10-x/2}(\text{PO}_4)_6(\text{OH})_{2-2x}(\text{CO}_3)_x$), or phosphate (PO_4^{3-}) sites as type B

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$(\text{Ca}_{10-x/2}(\text{PO}_4)_6-x(\text{CO}_3)_x(\text{OH})_2)$. These kind of carbonated apatite structures form a bioactive apatite with enhanced dissolution and osteoclast mediated resorption properties [6]. Furthermore, the incorporation of carbonate into the apatite structure leads to a decrease in crystallinity, a change in crystal morphology, and an enhancement of chemical reactivity due to the weak bonding due to carbonates geometry [7–9]. In fact, the carbonated apatite increases the local concentration of calcium and phosphate ions that are necessary for new bone formation [10]. For all these reasons, the production of CHAp and CFAp is of great value and has been extensively investigated using different synthesis processes such as precipitation, sol-gel, solid-state reaction, and hydrothermal treatment [11–17]. Mechanochemical activation as a simple and low cost method has been successfully employed to synthesis carbonated apatite, for example, CFAp [18,19] and CFAp/TiO₂ [20]. Furthermore, a number of bioceramics, for example, HAp [21], FAp [22], CAp [23], TCP [24], HAp/Ti [25], FAp/ZrO₂ [26], CAp/TiO₂ [27], CAp/ZnO [28], and CAp/Al₂O₃ [29] have been prepared by this technique. From a synthetic standpoint, the synthesis of nano-sized CHAp is typically based on the precipitation reaction developed by Nelson and Featherstone [30] and studied in detail by Barralet et al. [31,32]. Doi et al. also explored the influence of carbonate on sintering of apatites and indicated that the sintered CHAp can be resorbed by osteoclasts both under in vitro and in vivo conditions [33]. Moreover, it has been reported that A- and B-types CHAp can be synthesized by a high-temperature reaction of HAp with carbon dioxide gas and a precipitation reaction in liquid solution, respectively [34,35].

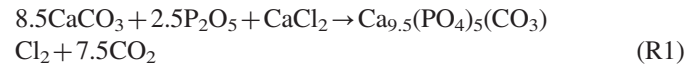
Even though a lot of research has been carried out concerning the preparation of CHAp and CFAp [36–38], the synthesis and characterization of n-CCAp utilizing mechanochemical method has not been reported so far. This article aims at investigating n-CCAp synthesis through a facile room-temperature mechanochemical reaction for the first time. The effect of high-energy ball milling has been evaluated with the purpose of recommending proper conditions for the mass production of n-CCAp nanopowders. Structural and morphological features of the product were also characterized by using XRD, FT-IR, SEM and TEM techniques. In addition, the mechanism of mechanical activation was proposed from the data obtained, to explain the possible reactions which had occurred during the milling process.

2. Experimental procedures

2.1. n-CCAp preparation

CaCO₃, P₂O₅ and CaCl₂ powders (all from Merck) were used as reactants for the mechanochemical synthesis of n-CCAp. The mole ratio of calcium to phosphorus was in accordance with the stoichiometric Ca/P content in the composition of n-CCAp which was equal to 1.67. The substitution degree of PO₄³⁻ by CO₃²⁻ was shown by the x value in the general formula of n-CCAp $(\text{Ca}_{10-x/2}(\text{PO}_4)_{6-x}(\text{CO}_3)_x\text{Cl}_2)$, where x value was chosen

equal to 1.0. Hence, the general form of the mechanochemical reaction (R1) is as follows:



Mechanochemical process was performed in a high-energy planetary ball mill using hardened chromium steel vials (vol. 125 ml) and balls (20 mm in diameter) under a high-purity argon atmosphere (99.99% purity) for 15, 180, 300, and 600 min. In all cases, the weight ratio of ball-to-powder (BPR), total powder mass, and rotational speed were 15:1, 7 g, and 600 rpm, respectively.

2.2. Characterization techniques

The phase analysis of the specimens was examined by X-ray diffraction (Philips X-ray diffractometer (XRD), $\text{Cu-K}\alpha$ radiation, 40 kV, 30 mA, 0.02 °S⁻¹ step scan, and 20° ≤ 2θ ≤ 70°). The following equation was used to determine the crystallite size and lattice strain of the products [39]:

$$B \cos \theta = \frac{0.9\lambda}{D} + \eta \sin \theta \quad (1)$$

where λ , D , η , and θ are the wavelength of the X-ray used (0.154056 nm), crystallite size, internal micro-strain, and the Bragg angle (°), respectively. Note that B in the above equation is the peak width (in radians) after subtracting the peak width due to instrumental broadening from the experimentally recorded profile. Therefore, when $B \cos \theta$ was plotted against $\sin \theta$, straight lines were obtained for samples with the slope as η and the intercept as $0.9 \lambda/D$.

If we assume that a crystallite is a sphere of diameter D surrounded by a shell of grain boundary with thickness t , the volume fraction of grain boundary (f) is approximately [18]:

$$f = 1 - \left[\frac{D}{(D+t)} \right]^3 \quad (2)$$

To determine the values of f , the obtained values of crystallite size was replaced with D under the assumption of $t=1$ nm. In addition, the crystallinity degree (X_c) was estimated by taking the sum total of relative intensities of individual characteristic peaks according to the following equation [18]:

$$X_c = \frac{\text{Sum}(I_1 : I_n)_{\text{CCAp}}}{\text{Sum}(I_1 : I_n)_{\text{Standard}}} \times 100 \quad (3)$$

The lattice parameters (a , b , and c) can be evaluated from the following relation

$$\frac{1}{d^2} = \frac{4h^2 + hk + k^2}{3a^2} + \frac{l^2}{c^2} \quad (4)$$

where h , k , and l are the Miller indices [18].

The unit cell volume (V) of n-CCAp was determined using the following equation [23]:

$$V = (a^2c)(\sin 60^\circ) \quad (5)$$

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