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Gradual mechanochemical reaction to produce carbonate doped fluorapatite–titania composite nanopowder

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Abstract

Carbonated fluorapatite–titania composite nanopowders were successfully synthesized by a facile room-temperature mechanochemical process. Mixtures of calcium carbonate, phosphorous pentoxide and calcium fluoride with different amounts of titania (0, 3, 6, and 9 wt%) were milled using a high-energy planetary ball mill for 10 h. Results showed that a gradual transformation occurred during the mechanical activation. In the absence of titania, nanosized B-type carbonated fluorapatite with crystallite size of 69 ± 3 nm was formed. In the presence of 3–9 wt% titania, mechanochemical reaction caused the formation of carbonated fluorapatite–titania composite nanopowders. The crystallite size declined drastically and reached 12 ± 1 nm when the titania content was increased to 9 wt%. In contrast, the lattice strain and volume fraction of grain boundary increased notably from 0.0045 ± 0.0002 to 0.0084 ± 0.0004 and from $4 \pm 0.21\%$ to $21 \pm 1.07\%$, respectively, while the titania content rose from 0 to 9 wt%. From the data obtained, the unit cell volume of carbonated fluorapatite was influenced strongly by the titania content, whereby the sharp increase in unit cell volume from 524.42 to 530.40 Å³ was due to the increase of the titania content from 0 to 9 wt%, respectively. Microscopic observations indicated that the product had a cluster-like structure with an average particle size of about 75 nm.

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1. Introduction

Bioceramics have always been considered as the most promising materials for hard tissue repair due to their superior biocompatibility and osteoconductivity [1,2]. Among the different forms of bioceramics, hydroxyapatite (HAp, Ca₁₀(PO₄)₆(OH)₂), fluorapatite (FAP, Ca₁₀(PO₄)₆F₂) and chlorapatite (CAp, Ca₁₀(PO₄)₆Cl₂) as well as carbonated apatite (CA, Ca_{10–x/2}[(PO₄)_{6–x}(CO₃)_x][(Z)_{2–2y}(CO₃)_y], Z=OH, F, Cl) have been considerably applied in biomedical applications as

potential bone-substitute materials [3,4]. It has been found that carbonated hydroxyapatite (CHAp) is a promising material for bone substitution as it is bio-resorbable and also more bioactive *in vivo* than stoichiometric HAp. These types of apatites are mostly used as powders and its usefulness depends on the powder features such as average particle size, surface area, and morphology. Nano-sized CHAp with a high surface area has interesting applications in various fields such as tissue engineering [5].

In general, the carbonate ion in hydroxyl and phosphate sites in the HAp lattice, termed as A-type (Ca_{10–x/2}(PO₄)₆(OH)_{2–2x}(CO₃)_x) and B-type (Ca_{10–x/2}(PO₄)_{6–x}(CO₃)_x(OH)₂) CHAp, respectively, can be replaced [6]. It has been found that B-type carbonated apatite has a very similar composition and structure to

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those of bone apatite, thus exhibiting higher bioactivity than pure HAp [7]. In addition, the substitution of OH^- groups by F^- ions in the HAp lattice causes an increase in the crystallinity degree and chemical stability as well as a decrease in the crystal strain [8,9]. On the other hand, the incorporation of titania (TiO_2) into apatites can improve their functional specifications due to its biocompatibility [10]. In fact, co-existence of apatite and TiO_2 enhances adhesion of coatings on substrate (Ti), provides a good combination of biochemical stability as well as mechanical properties in Ti-based implants [11–13]. This suggests that TiO_2 could be useful as reinforcing phase in calcium phosphate-based composites [14]. However, the previous studies showed that the phase compositions, structural features as well as morphological characteristics of the calcium phosphate-based composites may be influenced by the type and amount of reinforcing agents [15,16]. Therefore, the determination of the optimum amount of reinforcement is inevitable. Here, the preparation of carbonated fluorapatite-based composite nanopowder in the absence and presence of different amounts of reinforcing agent is the motivation for this study. From a synthetic perspective, the synthesis of nano-sized CHAp is mostly based on the precipitation reaction developed by Nelson and Featherstone [17] and studied in detail by Barralet et al. [18,19]. Doi et al. also studied the influence of carbonate on sintering of apatites and showed that the sintered CHAp can be resorbed by osteoclasts both under *in vitro* and *in vivo* conditions [20]. 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 [21,22].

Although various types of apatites are known, very few studies have been conducted on the preparation of CA-based composites [23]. Hence, in this study, the mechanochemical synthesis of carbonated fluorapatite–titania (CFAp– TiO_2) composite nanopowders as a severe plastic deformation (SPD) synthetic pathway is investigated. Depending on the mechanical activation circumstances, the milling processes fall into two class: gradual reaction (GR) [24,25] and mechanically induced self-sustaining reaction (MSR) [26,27]. In the first process, the reaction may extend to a very small volume during each collision, resulting in a progressive transition. In the second manner, a self-propagating combustion reaction can be initiated, if the reaction enthalpy is sufficiently high. To the best of our knowledge, this is the first study of mechanochemical synthesis of CFAP– TiO_2 composite nanopowders (GR mode). To determine the optimal amount of titania, the structural features of the samples in the absence and presence of different titania contents were examined. 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. Preparation of CFAP– TiO_2 composite

Fig. 1 displays a schematic view of the room-temperature mechanochemical process. In summary, commercial grade calcium carbonate (CaCO_3 , Merck, a mean particle size of

10–30 μm), phosphorous pentoxide (P_2O_5 , Merck, a mean particle size of about 100 μm), calcium fluoride (CaF_2 , Merck, an average particle size of 100 μm) and titanium dioxide (TiO_2 , Merck, a mean particle size of 3–5 μm) were used as the raw materials. All chemicals were used without purification. In accordance with the stoichiometric Ca/P ratio of B-type CFAP ($\text{Ca}_{10-x/2}(\text{PO}_4)_{6-x}(\text{CO}_3)_x\text{F}_2$), the mole ratio of calcium to phosphorus was equal to 1.9. The degree of substitution of PO_4^{3-} by CO_3^{2-} was demonstrated by the x value in the general formula of B-type CFAP, where x was equal to 1.0. To prepare the CFAP– TiO_2 nanocomposites, different values of titania (0, 3, 6, and 9 wt%) were mixed with the desired amounts of CaCO_3 , P_2O_5 , and CaF_2 and the blended powders were milled for 10 h in a high-energy planetary ball mill using hardened chromium steel vials (vol. 125 ml) and steel balls (20 mm in diameter) under a high-purity argon atmosphere (99.99% purity) at room temperature. The weight ratio of the ball-to-powder (BPR), total powder mass and rotational speed were 15:1, 7 g and 600 rpm, respectively. The stoichiometry for the overall reaction is as follows:

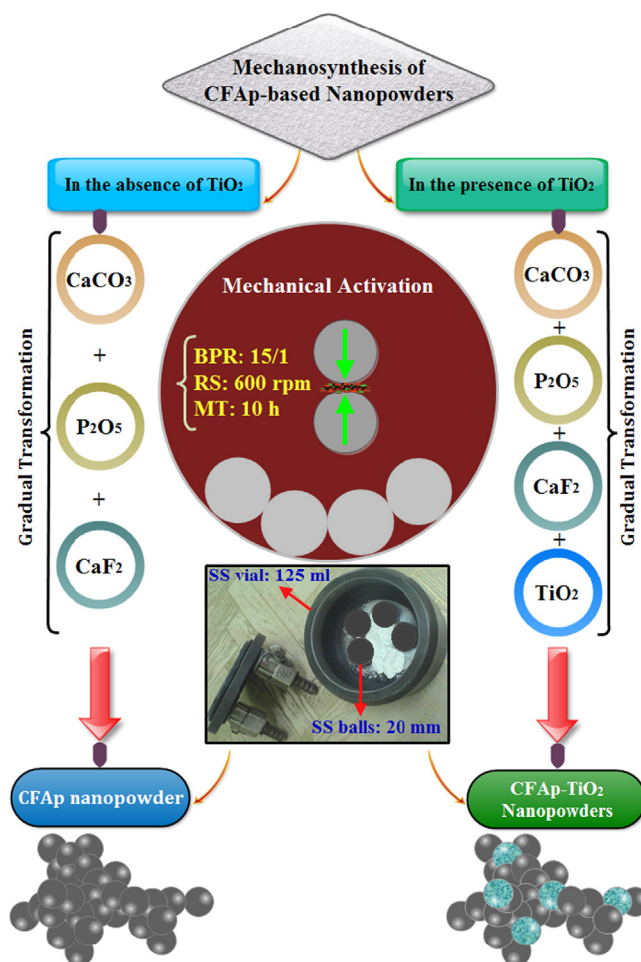
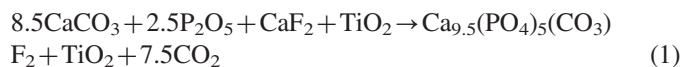


Fig. 1. A schematic view of the room-temperature mechanochemical process to produce carbonate doped fluorapatite–titania composite nanopowders.

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