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Characterization of single-crystal fluorapatite nanoparticles synthesized via mechanochemical method

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ABSTRACT

The synthesis of nanostructured fluorapatite (FA; $Ca_{10}(PO_4)_6F_2$) was explored from the starting materials of $CaHPO_4$, $Ca(OH)_2$, CaO, P_2O_5 and CaF_2 via a mechanochemical process. In this research, the suitability of using the mechanochemical process to prepare a high crystalline phase of FA was studied. The characterization and structural features of the synthesized powders were evaluated using powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) techniques. The results from the structural studies indicate that the maximum lattice disturbance in the apatite structure after the mechanochemical process was at the (0 0 2) plane. Furthermore, the maximum particle size was below the crystallite size after 60 h of milling and subsequent thermal treatment at 600 °C for 1 h (heated up to 600 °C and kept for 1 h at this temperature). We determined that this method gives rise to the single-crystal FA with an average size in the range of 25 ± 5 to 29 ± 9 nm. The present findings suggest that the solid-state reaction and appropriate thermal process simultaneously lead to the formation of nanostructured FA with spheroidal shape.

1. Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) has been used for biomedical applications because of its superior biocompatibility and bioactivity (Roeder, Converse, Leng, & Yue, 2006). Among the different forms of calcium phosphates, particular attention has been placed on HA because the bone mineral consists of tiny HA crystals (Kalita, Bhardwaj, & Bhatt, 2007). Nevertheless, HA has a high dissolution rate in biological systems (Fini et al., 2003), poor corrosion resistance in an acid environment and poor chemical stability at high temperature (Chen & Miao, 2005), which has restricted wider applications in the fields of orthopedics and dentistry.

The inorganic matrix of the bone is based on HA doped with different quantities of cations, such as Na^+, K^+ and Mg^{2+}, and anions, such as CO_3^{2-}, SO_4^{2-} and F^-. Among them, F^- plays a leading role because of its influence on the physical and biological characteristics of HA (Nikcevic et al., 2004). When fluoride (F) is consumed in optimal amounts in water and food and used topically in toothpaste, mouth rinses, and professionally applied office treatments, it increases tooth mineralization and bone density, reduces the risk and prevalence of dental caries and helps to promote enamel remineralization throughout life for individuals of all ages (Palmer & Anderson, 2001). Therefore, fluorine-substituted HA (FHA, $Ca_{10}(PO_4)_6(OH)_{2-x}F_x$) has attracted substantial attention as a clinical restoration material for improvement of the biostability of HA in biomedical applications (Fini et al., 2003). This substitution causes an increase in chemical stability, a decrease in mineral solubility, and a promotion in bone cell proliferation (Barinov, Shvorneva, Ferro, Fadeeva, & Tumanov, 2004; Jantova, Theiszova, Letasiova, Birosova, & Palou, 2008). If the OH^- in HA is completely substituted by F^-, fluorapatite (FA, $Ca_{10}(PO_4)_6F_2$) is formed. FA is found in dental enamel and is usually used in dental applications due to its greater mechanical strength. For all these reasons, the synthesis of FHA and FA is of great value and has been widely investigated by multiple techniques, such as precipitation (Chen & Miao, 2005), sol–gel (Cheng, Zhang, & Weng, 2006), hydrolysis (Kurmaev et al., 2002), hydrothermal (Rodriguez-Lorenzo, Hart, & Gross, 2003), and mechanochemical methods (Zhang, Zhu, & Xie, 2005).

Over the past decades, the mechanosynthesis process has been developed for the production of a wide range of nanostructured materials (Suryanarayana, 2001). The advantages of this technique are that melting is not necessary and that the powders are nanocrystalline (Silva, Graca, Valente, & Sombra, 2007). In general, the mechanochemical process can be performed under wet or dry conditions (Rhee, 2002; Silva, Pinheiro, Miranda, Goes, &

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Sombra, 2003). In most cases, the wet routes require precise controls on the processing conditions, and the characteristics of the final products are greatly influenced by various parameters. In addition, the synthesis procedure and apparatus are complicated. These difficulties lead to the synthesis of fluoridated HA with poor reproducibility and high processing costs, so it is not suitable for mass production (Rhee, 2002; Zhang et al., 2005). However, in the dry mechanosynthesis process, many of the difficulties are eliminated because the reactions are faster without the addition of water and a very low level of pollution by the mill material is observed (El Briak-BenAbdeslam, Ginebra, Vert, & Boudeville, 2008). Moreover, this process has the benefit of high reproducibility and low processing costs (Rhee, 2002). In most papers and patents concerning the synthesis of fluoridated HA, the mechanochemical process was performed (Fathi & Mohammadi Zahrani, 2009a, 2009b; Mohammadi Zahrani & Fathi, 2009; Silva et al., 2003), and only a few research groups have been devoted to the mechanochemical process and subsequent thermal treatment on FA bioceramic (Barinov et al., 2004).

The present work aims to synthesize nanocrystalline FA ($Ca_{10}(PO_4)_6F_2$) using novel solid-state processes that consist of the dry mechanochemical technique (to obtain nanostructured FA using high purity powders) and the thermal annealing process (for recovery of crystallinity degree of apatite powders). It was found that the control of the quality and crystallinity of apatite phases are important for improvement of their dissolution in the human body (Nakano, Tokumura, & Umakoshi, 2002). Therefore, studying the crystallinity, morphological characteristics and other structural features (crystallite size, lattice strain) of FA are important to understand its suitability for different biomedical applications.

2. Materials and methods

2.1. Preparation method

FA nanopowders with different structural characteristics were synthesized through novel dry mechanochemical processes, which are summarized in Fig. 1. The purpose of the milling was twofold: first, to activate the following reactions via mechanochemical processes, and second, to produce the nanostructured FA.

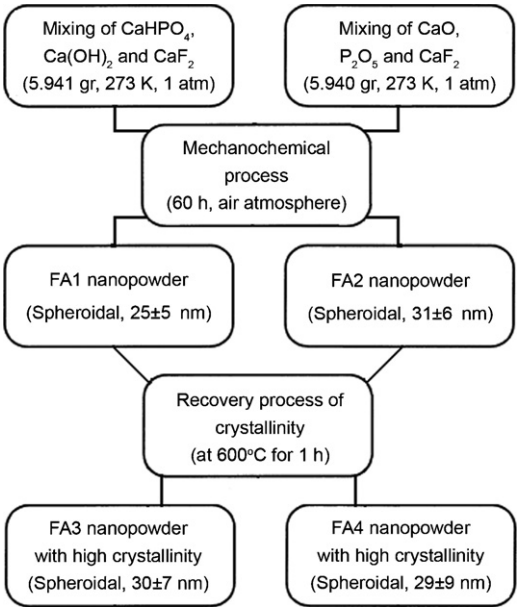

Fig. 1. Flow sheet of FA nanoparticles preparation.

The starting reactants were anhydrous dicalcium phosphate ($CaHPO_4$, Merck, Darmstadt, Germany), calcium hydroxide ($Ca(OH)_2$, Sigma–Aldrich Corporation, St. Louis, USA), phosphorous pentoxide (P_2O_5, Merck, Darmstadt, Germany), calcium oxide (CaO, Merck, Darmstadt, Germany) and calcium fluoride (CaF_2, Merck, Darmstadt, Germany). To synthesize the nanostructured FA, the initial powders were ground on a high energy planetary mill with the stoichiometric proportionality between the materials given in following reactions:

$$6CaHPO_4 + 3Ca(OH)_2 + CaF_2 \rightarrow Ca_{10}(PO_4)_6F_2 + 6H_2O \quad (I)$$

$$9CaO + 3P_2O_5 + CaF_2 \rightarrow Ca_{10}(PO_4)_6F_2 \quad (II)$$

Milling processes were performed in polyamide 6 vials (150 mL) using zirconia balls (diameter 20 mm) under ambient air atmosphere. The charge-to-ball ratio and rotational speed were 1:20 and 600 rpm, respectively. To prevent excessive heating, the milling was carried out in 45-min milling steps with 15-min interval pauses. The subsequent thermal annealing process was performed in an electrical furnace at 600 °C for 1 h in air.

2.2. Characterization

Phase analysis and structural transformation were evaluated with the Philips X-ray diffractometer (XRD) with Cu Kα radiation. The diffractometer was operated at 40 kV and 30 mA. All measurements were performed at room temperature, 25 °C, within a diffraction range of $2\theta = 0–60^\circ$ at 1°/s speed. PANalytical X'Pert HighScore software (Almelo, The Netherland) was also used for the analysis of different peaks. The diffraction patterns of products were compared to standards proposed by the Joint Committee on Powder Diffraction and Standards (JCPDS), which involved card # 15-0876 for FA, # 24-0033 for HA, and # 09-0080 for $CaHPO_4$.

The functional groups of fine powders were examined using Fourier transform infrared spectroscopy (FT-IR: Bruker, TENSOR27). One milligram of the powdered sample was mixed with 200 mg spectroscopic grade KBr by hand-milling the powder in an agate mortar. Subsequently, the transmittance spectrum was recorded in the range 4000–400 cm^{-1} at 2 cm^{-1} resolution by 16 scans.

Scanning electron microscopy (SEM, SERON AIS-2100) was applied to characterize the morphological characteristics of the samples, which were sputter-coated with a thin layer of gold with a PVD apparatus (Fathi & Hanifi, 2007). The accelerating voltage and vacuum control were 20 kV and fully automated, respectively. Energy dispersive X-ray spectroscopy (EDX), which was coupled with SEM, was used for semi-quantitative examination of the samples (voltage used for EDX equal to 20 kV).

A dilute suspension of the powders obtained in ethanol were collected on carbon-coated copper grids and allowed to dry for 3 min. The size and morphology of fine powders were observed in a transmission electron microscope (Philips CM10, Eindhoven, The Netherlands) operated at 100 kV.

3. Results and discussion

3.1. XRD analyses

In Fig. 2(a) and (b), XRD patterns of the FA1 and FA2 samples are shown, respectively, showing that the powders synthesized through the two different mechanochemical processes are mostly FA. The JCPDS reference 15-0876 was used, and major peaks between $2\theta = 20–60^\circ$ were obtained. The peaks at $2\theta = 25.86$, 31.94, 32.27, 33.13, 34.14, 40.04, 46.87, and 49.58° were compared and