

Synthesis and solubility of calcium fluoride/hydroxy-fluorapatite nanocrystals for dental applications

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Abstract

As the mineral phase of tooth enamel consists of apatite containing fluoride, the “CaF₂-like” salts are of significant interest in dentistry for their roles as labile fluoride reservoirs in caries prevention. Fluoride ion is required for normal dental development because of its therapeutic ability of osteoporosis healing and stimulating osteoblast activity both *in vitro* and *in vivo*. In this research, biphasic Calcium fluoride/fluorinated-hydroxyapatite (CF/FHAp) nanocrystals have been successfully synthesized via co-precipitation method. The synthesized powder was characterized by the commonly used bulk techniques such as chemical analysis, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray powder diffraction (XRD) analyses. The obtained results confirmed the formation of biphasic powder composed of about 46% CF and 54% (w/w%) apatite phase which was a solid solution composed of more than 50% fluorapatite (FAp). In addition, *in vitro* evaluations of the powder were performed, and for investigating their bioactive capacity they were soaked in simulated body fluid (SBF) at different time intervals. The samples showed significant enhancement in bioactivity within few hours of immersion in SBF solution. Also, the EDS analysis clearly showed dissolution and deposition of calcium and phosphate ions on the surface of synthesized biphasic powder after the first week of immersion in SBF solution.

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1. Introduction

Synthetic hydroxyapatite (HAp) has been used extensively as a bone implant material due to its identical chemical composition and high biocompatibility with natural bone [1–3]. The inorganic matrix component of natural bone is based on HAp with formulation of Ca₁₀(PO₄)₆(OH)₂ doped with different quantities of cations like Na⁺, K⁺ and Mg²⁺ which occupy Ca²⁺ sites and anions such as CO₃³⁻, SO₄⁴⁻ and F⁻ substituting OH⁻ groups. According to the previous studies, these dopants especially F⁻ have a great influence on the physical and biological properties of the material [4,5]. There are also various FHAPs with different degrees of fluorination, Ca₁₀(PO₄)₆(OH)_{2-2x}F_{2x} (*x* is the degree of fluorination, *x* = 0 HAp, *x* = 1.0 FAp, 0 < *x* < 1 forms FHAp solid solution). Fluorine tends to reduce the crystal size and increases stability

of the apatite structure. At lower degrees of fluorination the apparent solubility declines markedly. It was suggested that FHAp has a better thermal and chemical stability than HAp [6]. This phenomenon which was described well by Elliott *et al.* [7] could be explained by considering the crystal structure of apatites. When a certain amount of F⁻ ions substituted with the OH⁻ groups in the HAp matrix, a certain level of chemical and thermal stability of the FHAp ceramics will be achieved. Theoretically, F⁻ ion concentration of 50% in the FHAp would be enough to remove the disorder of the crystal structure of HAp and hence stabilize its structure due to the alternating arrangement of the F⁻ ions between each pair of OH⁻ groups. However, by considering the random substitution of OH⁻ ions with F⁻ ions in the OH⁻ positions, the F⁻ ion concentration required for stabilizing the structure was necessarily higher than 50% [1]. Thus, FHAp exhibits a considerable combination of stability and biocompatibility [6].

Additionally, fluoride is an essential trace element required for normal dental and skeletal development. It has been shown that the presence of fluoride possesses beneficial effects on

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increasing the quantity and quality of bone formation in the body [8]. Thus, the bone mineral produced by FAp is less susceptible to dissolution and possible resorption. The fluoride ion has a therapeutic ability for healing of osteoporosis, since the bone mass is increased with F⁻ ion administration [9]. F⁻ ion is known to stimulate osteoblast activity both *in vitro* and *in vivo*. In addition, the mineral phase of tooth enamel consists of apatite containing 0.04 wt. % to 0.07 wt. % of fluoride, and constitutes about 95 to 97% of the dry mass. F⁻ ions present in saliva and blood plasma, are required for normal dental and skeletal development. It has been suggested that intaking fluoride of about 1.5–4 mg/day significantly reduces the risk of dental caries [10]. Owing to the fact that fluoride is well known for caries prevention and treatment of osteoporosis, FAp has been widely investigated [6,7,9–19].

CF and “CaF₂-like” materials are also of significant interest in dentistry due to their roles as labile fluoride reservoirs in caries prevention. Low concentration of F in oral fluids derived from labile F⁻ reservoirs formed by the use of F⁻ dentifrices and rinses has been shown to have profound effects on the progression of dental caries [20–22]. However, the low Ca concentration in the mouth provides a limited driving force for the formation of CaF₂, and only very small amounts of CaF₂-like deposits are formed after a conventional sodium fluoride rinse [23]. Precipitation of CaF₂ can cover the entire surface of hydroxyapatite when supplied at a sufficiently high concentration [24]. Previous studies showed that a two-solution delivery system, which supplies both F and Ca in a way that leads to homogeneous nucleation and formation of very small CaF₂ crystals in the mouth during application, was highly effective in increasing deposition and retention of labile F in the mouth [25,26]. This, in turn, increased the remineralization effects of the F regimen without increasing the F levels [27,28].

There are several methods of synthesizing HAp and FHAp with varied fluorine contents, such as, precipitation [29,30], sol-gel [31] a solid state reaction [32], and pyrolysis methods [33]. Also, CF powder was synthesized by different methods such as sol-gel method [34–36], solvothermal process [37,38], reverse micelle method [39,40], different precipitation methods [41–44], flame synthesis [45] and spray-drying process [46]. Among the methods mentioned above, precipitation method appears to be the most widely used for both FHAp and CF bioceramics.

The present study was aimed at preparing biphasic CF/FHAp solid solution through a continuous precipitation method especially for dental applications, which could be used not only as an osteoconductive material due to the nature of FHAp but also, as a labile F⁻ reservoir for developing potentially more effective F⁻ regimens and as an agent for use in the reduction of dentin permeability and dental caries prevention.

2. Materials and methods

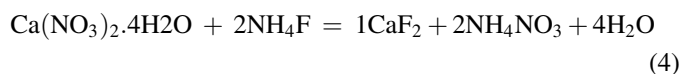
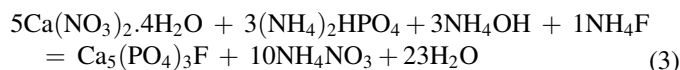
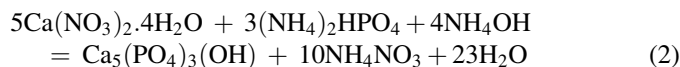
2.1. Synthesis of biphasic powder

In a typical experiment, 0.03 M diammonium hydrogen phosphate solution [(NH₄)₂HPO₄, %99, Merck; No.1207], 0.05 M calcium nitrate 4-hydrate solution [Ca(NO₃)₂ · 4H₂O,

%98, Merck PROLABO; No.22 384.298] and a mixed solution containing 0.03 M ammonia(NH₃, Merck; No. 1.05426) with 0.01 M ammonium fluoride(NH₄F, Merck; No. 101164) were prepared. The latter solution was a buffer solution in which its pH can be measured by the following equation (1):

$$\text{pH} = 9.24 + \text{Log} \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \quad (1)$$

Therefore, the value of the obtained pH was 9.72. This buffer solution was used to simultaneously provide fluoride ion and also keeping pH at a constant value for synthesizing proper product. Required volume of buffer solution was added to both solutions to adjust their pH on 9.72. Afterward, phosphate solution was added drop-wise into calcium nitrate solution, at ambient temperature, resulting in the precipitation of a biphasic powder. During reaction, pH of the reactor was maintained on initial value by continuous adding of buffer solution. The precipitation of product can be described by simultaneous reactions leading to apatite phase. It could be HAp (Eq. 2) or FAp (Eq. 3) or the reaction which leads to CF (Eq. 4) as follow:



The precipitate was centrifuged and washed with de-ionized distilled water. The processes of centrifuging and washing were carried out twice. The obtained powder was dried in a lyophilizer system (Alpha 1–2LD, Germany) overnight. The schematic flowchart of the synthesis procedure is shown in Fig. 1.

2.2. Preparation of SBF solution

The SBF solution was prepared by dissolving reagent-grade NaCl, KCl, NaHCO₃, MgCl₂ · 6H₂O, CaCl₂ and KH₂PO₄ into distilled water and buffered at pH = 7.25 with TRIS (tris(hydroxymethyl) aminomethane) and 1 M HCl solution at 37 °C. Therefore, concentration of Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, HCO₃⁻, HPO₄²⁻, SO₄²⁻ ions in the prepared SBF solution was 142.0, 5.0, 1.5, 2.5, 147.8, 4.2, 1.0 and 0.5 mmol/dm³, respectively. It should also be noted here that SBF is a solution highly supersaturated with respect to apatite [47].

2.3. Characterization

2.3.1. SEM observations

The microstructure of the prepared samples was examined by SEM. For this aim, the samples were coated with a thin layer of Gold (Au) by sputtering (EMITECH K450X, England) and then the microstructure and morphology of them were evaluated by SEM (Philips XL30) that operated at the acceleration voltage of 15 kV.

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