

Sol-gel synthesis of FHA / CDHA nanoparticles with a nonstoichiometric ratio

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Abstract

The aim of this study was to investigate the sol gel synthesis of HA/FA nanoparticles and the possible formation of TCP phase or unstoichiometric calcium deficient hydroxyapatite (CDHA) from the precursors with a Ca/P ratio of 1.62. In order to prepare the sol, the solutions of Triethyl phosphite, ammonium fluoride and calcium nitrate in ethanol were used respectively as P, F and Ca precursors. The crystallinity, particle and crystallite size, powder morphology, chemical structure and phase analysis were investigated by SEM, XRD, FT-IR and Zeta sizer experiment. A multiphase compound containing hydroxyapatite (HA) and fluoroapatite (FA) nanoparticles and calcium deficient hydroxyapatite (CDHA) agglomerates was obtained. The size of the crystallites estimated from XRD patterns using Scherrer equation and the crystallinity of HA phase were about 5 nm and 66% respectively. The zeta sizer experiments for the dispersed particles in its own conditions showed an average size of 98 nm.

Keywords: *Sol-gel, fluor-hydroxyapatite, calcium deficient hydroxyapatite, nanoparticles*

1. Introduction

Hydroxyapatite [HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] is one of the types of calcium phosphates, which has extensive applications in the healing of bone and tooth, due to biocompatibility and similar composition to that of natural bone [1,2]. Pure fluorapatite [FA, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$] has more chemical and structural stability in comparison to HA[3,4]. HA has more chemical and structural stability and lower resorption kinetics in comparison to several calcium phosphate phases such as α -TCP ($\text{Ca}_3(\text{PO}_4)_2$) and TTCP ($\text{Ca}_4\text{P}_2\text{O}_9$) under physiological Conditions [5]. The calcined dense HA implants especially of high crystallinity does not show a significant sign of biodegradability in vivo even years after implantation. There are even reports about the formation of thick fibrous layer which is considered as a negative

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response of surrounding tissue to implant [6]. Regarding the characteristics of HA and α -TCP, a composition of these two phases (BCP) is considered to be more bioactive and more efficient than HA alone for the repair of bone defects. In the recent years, less chemically stable compounds such as BCP, CDHA, ACP and bioglass have been widely investigated for cellular as well as growth factor-based tissue engineering [7,8]. In this study, the sol-gel processing was used to synthesize the calcium phosphate powders. The advantages of sol-gel method over other methods are precise control of composition, low processing temperature, better homogeneity etc [9,10]. Taking into account the role of chemical composition, choosing the Ca/P ratio of less than 1.67 in the starting materials might be considered as an alternative to investigate in-situ preparation of the powders containing bioactive TCP/CDHA/FHA nanoparticles. The company of chemical composition factor to control the bioactivity and feasibility of preparing very fine particles increases the hope for the production of suitable bioactive powders for dental tissue applications.

2. Materials and methods

In order to prepare the sol, the solutions of (TEP, $[(C_2H_5O)_3P]$; Merck), (NH_4F ; Merck), ($Ca(NO_3)_2 \cdot 4H_2O$; Merck) in ethanol were used respectively as P, F and Ca precursors with a nonstoichiometric Ca/P ratio equal to : 1, 1/5, 1/62, 1/72.

First, NH_4F was added to TEP in ethanol (P/F=6) and in a separate container, calcium nitrate tetrahydrate was dissolved in ethanol. The resulted solutions were vigorously agitated for 24 h. Subsequently, the Ca containing solution was added to the P containing one. The resulted sol was kept at room temperature for 72 h and then aged at room temperature for a period of 24 h. The samples were dried at $70^\circ C$ for 3 days and heat treated at $550^\circ C$ for 1 h.

Microstructural characteristics, powder morphology, particle size, chemical structure and phase analysis were performed by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FT-IR) and Zetasizer experiments.

3. Results and discussion

The results of X-ray diffraction and Fourier Transform Infrared spectroscopy (FT-IR) of powder sample are shown in the [Figures 1](#) and [2](#) respectively.

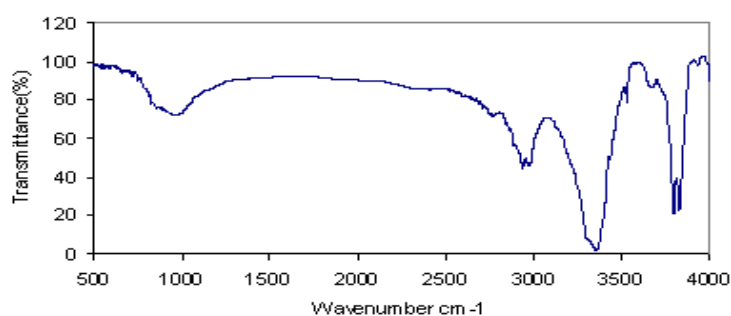


Fig.1. FT-IR patterns of the powder sample

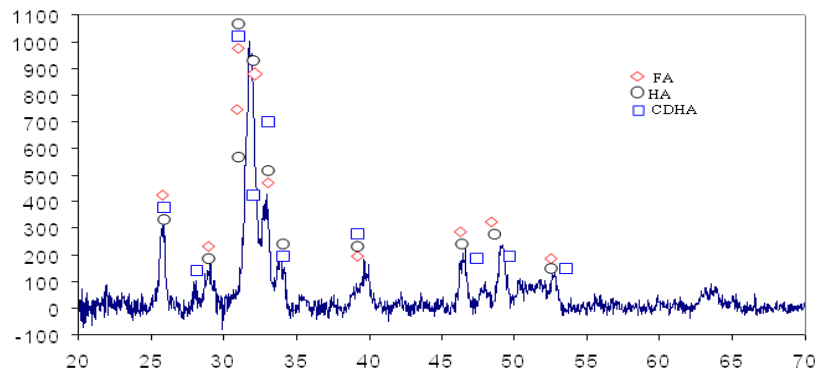


Fig.2. X-ray diffraction pattern of the powder sample

The typical characteristic P-O bands of apatite structure in the range of 550–610 and 950–1100 cm^{-1} were identified. The peak in 3550 cm^{-1} indicates the presence of hydroxyl group appeared due to hydrogenic bond with fluoride ions. The presence of carbonate group in 1420-1453 cm^{-1} shows the sample is carbonated. The similar results are obtained by Kim *et al.* [11] and Anastasios *et al* [12] for the synthesis of HA/FA from stoichiometric Ca/P ratio.

The characteristic peaks of apatite in the range of $2\theta=25-35^\circ$ was identified in the XRD pattern. This pattern showed the powder sample was not perfectly crystalline and composed of HA, CDHA and FA. Despite of Ca/P ratio of 1.62 used in this study, no trace of β -TCP and α -TCP was identified. In the equilibrium condition, a TCP amount of 54% is deduced from the CaO- P_2O_5 phase diagram for a given Ca/P ratio of 1.62.

The degree of HA crystallinity was calculated via equation below [13]:

$$1. \quad X_C = 1 - (V_{112/300} - I_{300})$$

In this equation, X_C is the degree of crystallinity, $V_{112/300}$ is the depth of the valley between the characteristic peaks corresponding to the planes of (112) and (300) and I_{300} is the intensity of (300) planes. The size of the crystallites estimated from XRD patterns using Scherrer equation and the crystallinity of HA phase were about 5 nm and 66% respectively.

The SEM image of powder sample is shown in the Figure 3. The EDAX analysis (Figure 4) revealed the phase composition of granular nanoparticles (zone A) and nongranular smooth agglomerates (zone B) could be HA/FA and CDHA respectively. The similar HA/FA particle morphology was obtained for the stoichiometric Ca/P ratio elsewhere [11].

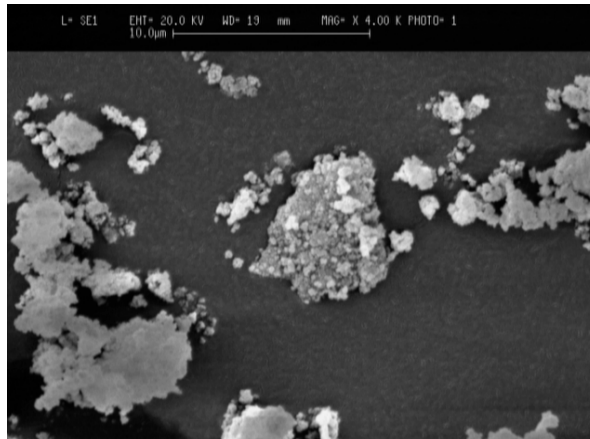


Fig.3. SEM image of powder sample.

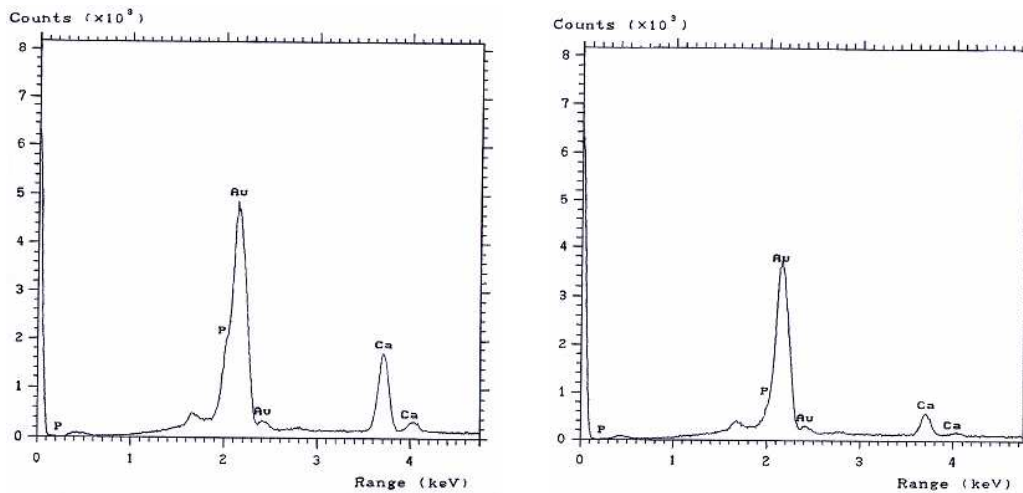


Fig.4. EDAX analyses of zone A. (left) and zone B. (right).

Considering the SEM image, it seems the agglomerates were sufficiently dispersed in the Zeta sizer testing conditions. The Zeta sizer experiments for the dispersed particles in its own conditions showed particle sizes ranging from 90 to 180 nm with an average size of 98 nm.

4. Conclusion

Phase characterization and chemical structure analyses confirmed the presence of apatite phases (Flourapatite and hydroxyapatite) and calcium deficient hydroxyapatite (CDHA). Despite of the Ca/P atomic ratio equal to 1.62 used in this work, no trace of tricalcium phosphate was identified. FT-IR analysis revealed also that the FHA was slightly carbonated. The crystallinity of HA component estimated by XRD was found to be about

66%. Very fine distribution of the nanosized FHA grains as well as the calcium deficient hydroxyapatite agglomerates were identified in the SEM studies. XRD-based estimation revealed the crystallite sizes were about 5 nm. The Zeta sizer experiments for the dispersed particles in its own conditions showed an average size of 98 nm.

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