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Synthesis, characterization, of Fluorohydroxyapatite nanopowders by sol-gel processing

ABSTRACT

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In this work, sol-gel processing was used to synthesize the fluorohydroxyapatite (nano-FHA, $Ca_{10}(PO_4)_6(OH)_{2-x}F_x$) nanopowders. The advantages of the sol-gel method over other methods are precise control of composition, low processing temperature, and better homogeneity. Calcium nitrate tetrahydrate, phosphorous pentoxide and Tetrabuthylammonium fluoride were used, respectively, as P, Ca, and F precursors with a Ca:P ratio of 1.67. The FHA powders were calcined at temperatures of 600ºC. The characterization and structural features of the synthesized powders were evaluated using powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) spectra and scanning electron microscopy (SEM) techniques. The thermal stability of FHA powders was studied through diffraction thermal analysis (DTA) and the optimized calcination temperature was found 600ºC, we used thermal gravimetric analysis (TGA) experiment in three heating rate 7, 10, 15 (ºC) on minute. The in vitro behavior of powder was investigated with mouse fibroblast cells.

Keywords: *Fluorohydroxyapatite; Nanopowders, Sol-gel; Synthesize; X-ray diffraction (XRD); Scanning electron microscopy (SEM).*

INTRODUCTION

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Synthetic hydroxyapatite, [HA, $Ca_{10}(PO_4)_6(OH)_2$], has been extensively used as an implant material for bone substitute owing to its excellent osteoconductive properties [1]. Among the different forms of calcium phosphates, particular attention has been placed on HA because the bone mineral consists of tiny HA crystals [2]. Nevertheless, HA has a high dissolution rate in biological systems [3], poor corrosion resistance in an acid environment and poor chemical stability at high temperature [4], which has restricted wider applications in the fields of orthopedics and dentistry.

It is believed that the reason for fluoride's anticaries effect is due to its ability to partly transform the carbonated hydroxyapatite in enamel to thermodynamically more stable FA or fluorhydroxyapatite (FHA), and then during the caries process, the fluoride is released, which changes the dynamics of the demineralization/remineralization process [5]. The substitution of OH^-, Cl^-, CO_3^{2-}, or other ions for the F^- usually leads to atomic displacements and lower symmetry, therefore compromising its chemical stability [6]. When OH^- groups in HA are partially substituted by F^-, fluorine substituted hydroxyapatite, [FHA, $Ca_{10}(PO_4)_6 (OH)_{2-xFx}$, $0 < x < 2$], is obtained [7]. The presence of fluorine (F) in saliva and blood plasma is important for normal skeletal and dental development. It has been suggested that fluorine intake of 1.5–4 mg/day significantly reduces the risk of dental caries [7]. Bioactivity of this materials will be able them to make direction bond with damaged texture. Hydroxyapatite properties such as bioactivity, mechanical strength, solubility and capability properties can be optimum from method of chemical composition control, morphology and the grains size control [8].

Iran. Solution of Hydroxyapatite can be control by many so factors for example: rate of crystallization, chemical composition and elements stoichiometry ratio [7]. Many methods, namely, solid-state reaction, wet precipitation and sol–gel processing have been developed for the preparation of FHA powders and ceramics [9-11]. One of the most common methods for the synthesis of fluorhydroxyapatite is the sol-gel method.

In this work, we have used Tetrabuthylammonium fluoride ($N(C_2H_4)_4F$) as the fluorine reagent for the preparation of FHA but in several past studies Hexafluorophosphoric acid (HPF_6) has been used as the fluorine reagent [12-14]. The excellent biocompatibility of HA nanostructures has resulted in many studies focusing on their synthesis [15-20]. This is mainly achieved by using surfactants [15], glutamic acid [16], EDTA [17], polyaspartate [18], biological proteins [19], etc. However, there is little literature specially reporting the synthesis of 1-dimension fluorapatite nanostructures. In comparison to hydroxyapatite, the incorporation of fluoride makes the fluorapatite structure more stable, therefore, the reaction progresses more easily under relatively simple and mild reaction conditions.

EXPERIMENTAL

Materials and instruments

Analytical grade Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, Merck, Germany), phosphorous pentoxide (P_2O_5, Merck, Germany) and Tetrabuthylammonium fluoride [($N(C_2H_4)_4F$) DAP, Merck, Germany], were used as precursor materials for the preparation of nanocrystalline FHAs. IR spectra were recorded by using the KBr disks on a Brucker tensor (model 420) spectrophotometer. Structural characterization of the samples by XRD measurements was carried by an equipment with Cu target of $\lambda k_\alpha = 1.540A$. Absorbance and also photoluminescence from the prepared samples was taken by a V-570 UV and Cary 4000 systems, respectively. SEM images were achieved by FESEM: S-4160: HITACHI.

Synthesis of nano-fluorohydroxyapatite

Nano-FHA was synthesized using an ethanol based sol–gel technique similar to previous reports of FA and FHA sol–gel coatings/powders manufacture. Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) was dissolved in ethanol (Merck) at a concentration of 2 mol l_1 as a Ca precursor solution and phosphorus pentoxide (P_2O_5) was dissolved in ethanol at the concentration of 2 mol l_1 as a P precursor solution and refluxing process for 12 h to obtain a clear P-containing solution. P, F, and Ca precursors with a nonstoichiometric Ca:P ratio equal to 1:67. First, Tetrabuthylammonium fluoride (P/F=6) was added to P_2O_5 in ethanol to form the P–F mixture. Subsequently, the solution containing Ca was added to the solution containing P. The resulting solution was refluxed for 48 h to obtain the FHA solution. The FHA solution was dried at 120 ºC for 12 h. The FHA powders were calcined at temperatures of 600ºC.

The powders were subjected to various investigations using experimental techniques like XRD for the phases present and crystal size measurement, FT–IR and SEM for the particle size and morphology.

X-ray Diffraction Analysis (XRD)

X-ray diffraction (XRD) technique was used to determine the ingredients of the sample. The morphology of nano composite was observed using a scanning electronic microscopy (SEM). For

SEM analysis, the powder sample was ultrasonically dispersed in ethanol to form dilute suspensions and then a few drops were deposited on the carbon coated copper grids.

Fourier Transform Infrared Spectroscopy (FTIR)

FT–IR spectra were obtained over the region 450–4000 cm^{-1} in pellet form for 1 mg powder samples mixed with 200 mg spectroscopic grade KBr (Merck, Germany). Spectra were recorded at 4 cm^{-1} resolution averaging 80 scans. Fourier Transform Infrared spectroscopy (FT-IR) of powder sample is shown in the Figure 1.
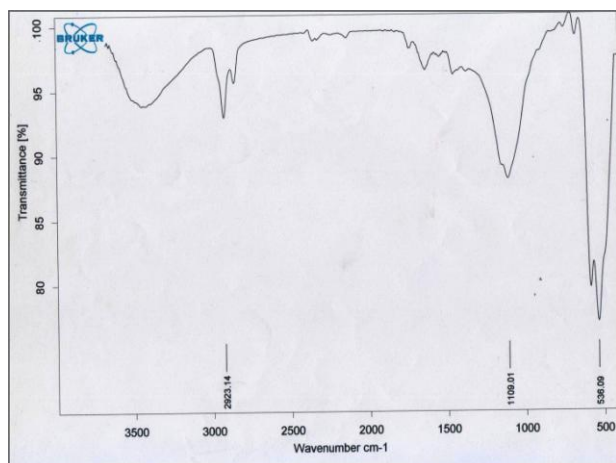

Fig. 1. FTIR spectrum of nano- fluorohydroxyapatite.

RESULTS AND DISCUSSION

Room temperature powder X-Ray diffraction spectra for the product was performed to identify the crystalline phase present in the sample and shown in Figure 2. The broadening of the peaks indicated that the particles were of nanometer scale. The average crystallite size (Dc) of the FHA nano composite was calculated using the Debye-Scherrer Equation (1) from the major diffraction peaks of the corresponding (002) and (111).

$$D_c = K.\lambda / \beta.\cos\theta \quad (1)$$

Where K is a constant equal to 0.9, λ is the X-ray wavelength (0.15405 nm), β is the full width at half maximum (FWHM) of the diffraction peak in radiant and θ is the Bragg angles of the main planes. The XRD peaks were markedly broader, which suggested that particles were

nanosized. The average crystallite size of the FHA nano composite was 50 nm, in agreement with that observed from SEM images (Figure 3).

FTIR absorption was used in order to check the characteristic bands of the synthesized nano fluorohydroxyapatite. Figure 1 shows the FT–IR spectra of FHA powder subjected to heat-treatment at 600 ºC for 2 h.
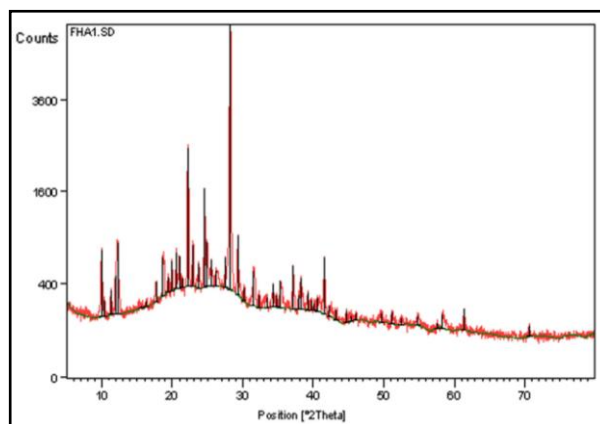

**Fig. 2.** XRD plot of an undoped sample of nano- fluorohydroxyapatite.

Fig. 3. SEM images of nano- fluorohydroxyapatite.

The characteristic bands (listed in Table 1) exhibited in the FHA spectra are assigned here: The band at 3470 cm^{-1} due to the stretching mode of hydrogen-bonded OH– ions, OH…OH and OH…F, respectively. The 536 cm^{-1} arise from vibrational mode of OH$^-$ ions. The bands at 1109 cm^{-1} and 1114 cm^{-1} arise from υ_3 PO$_4$, the band at 962 cm^{-1} arise from υ_1 PO$_4$. The band at 730 cm^{-1} arises from CO$_3$ ions.

At the Figure 4 (TGA) curve show the Flourapatite kinetic. With attention to the curve observed that in the temperature between 75ºC until 800ºC we have differed in slope.

Table 1. Infrared bands assigned for FHA

Assignment	Infrared frequency (cm^{-1})
$\upsilon_4 PO_4^{3-}$ bend	705
OH$^-$ (librational)	536
CO_3^{2-}	730
$\upsilon_1 PO_4^{3-}$ (stretching)	1380
$\upsilon_3 PO_4^{3-}$ (stretching)	1109 1114
OH$^-$ (stretching)	3470
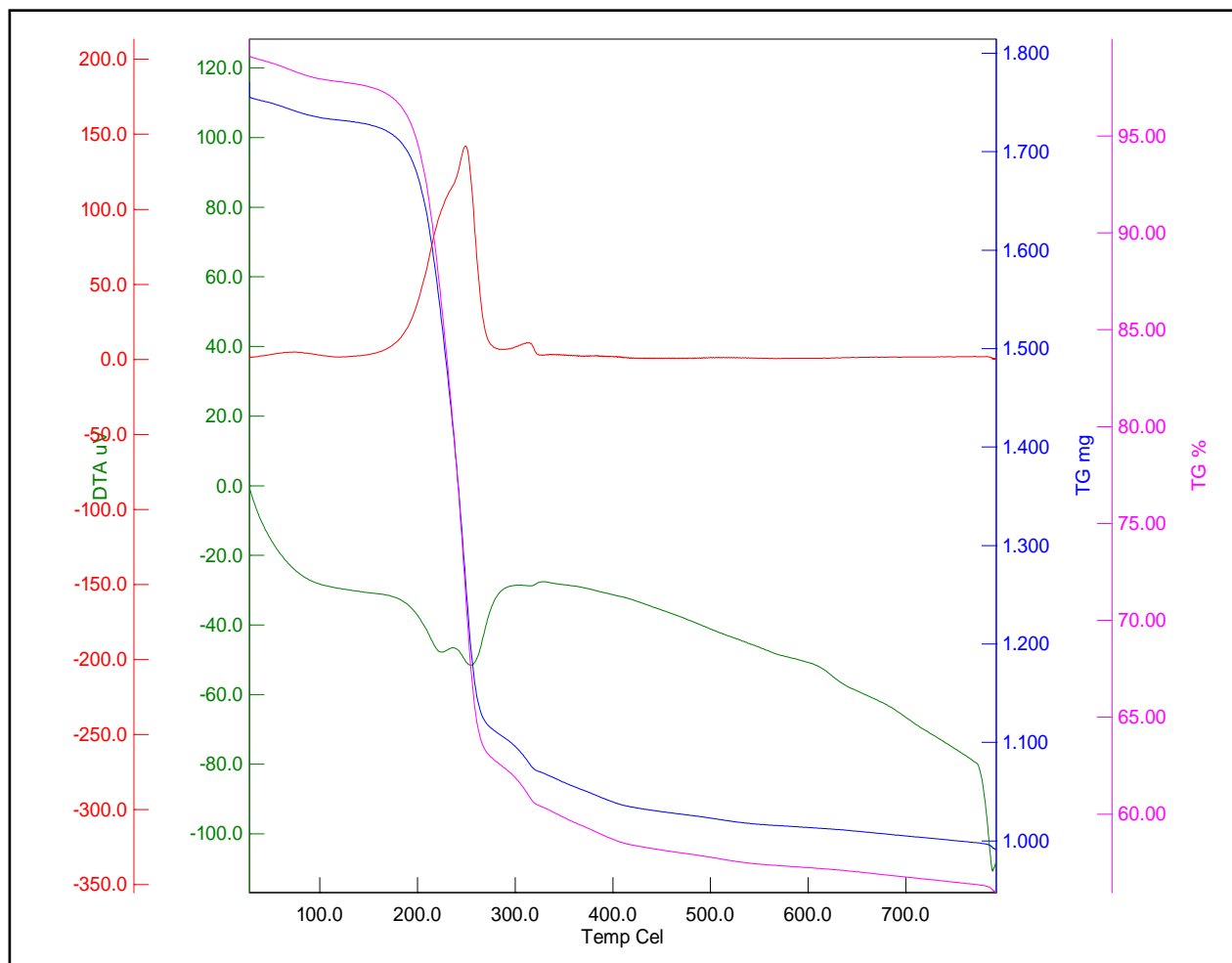
Fig. 4. TGA spectrum of nano- fluorohydroxyapatite.

CONCLUSIONS

Nanocrystalline fluorine-substituted hydroxyapatites (FHAs) were successfully synthesized by sol-gel method. The FT–IR spectroscopic results suggest that the fluoride substitutes for the hydroxyl groups. The SEM micrographs show that the particles are of 50 nm size and the morphology has been slightly changed with increase in fluoride ion substitution in the microwave synthesized FHAs.

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REFERENCES

[1] Groot K., (1980), Bioceramics consisting of calcium phosphate salts. *Biomat*.1: 47-50

[2] Kalita S. J., Bhardwaj A., & Bhatt H. A., (2007), Nanocrystalline calcium hosphate ceramics in biomedical engineering. *Mat.Sci. and Eng*.27: 441-449.

[3] Kenny S M., and Buggy M., (2003), Bone cements and fillers: a review. *J. Mater. Sci. Mater. Med.* 14: 923-938.

[4] Pullen L J and Gross K A., (2005), Dissolution and mineralization of sintered and thermally sprayed hydroxy-fluoroapatites. *J. Mater. Sci. Mater. Med*. 16: 399-404.

[5] Clarkson B. H, (1991), Caries prevention-fluoride. *Adv. Dent. Res*. 5: 41-45.

[6] Smith, DK, Brown PW., Constantz B., editors. Boca Raton, FL., (1994), Hydroxyapatite and Related Materials. *CRC Press*. p. 29

[7] Rameshbabu N., Sampathkumar T S., and Prasad Rao K., (2006), Synthesis of anocrystalline fluorinated hydroxyapatite by microwave processing and its in vitro

dissolution study. *Bull. Mater. Sci*. 29: 611–615.

[8] Zahraei M., fathi A., (2008), the effect of heat treatment on amount of crystallization and flourapatit nano powder composition that had produced with sol-gel method, the ninth surface engineering & heat treatment, *Iranian Veter. Res. J.*, 64: 47-54.

[9] Jha L. J. et al., (1997), Preparation and characterization of fluoride-substituted apatites. *Mater. Sci. Mater. Med*. 8:185-191.

[10] Rodriguez-Lorenzo L. M., Hart J. N., Gross K. A., (2003), Influence of fluorine in the Biomaterials, *Biomat.,* 24: 3777-3785.

[11] Okazaki M., Tohda H., Yanagisawa T., Taira M., (1998), Differences in solubility of two types of two types of heterogeneous fluoridated hydroxyapatites. *Takahashi J., Biomat.*19: 611-616.

[12] Cheng K. et al., (2003), Sol–gel derived fluoridated hydroxyapatite films. *Mater.Res.Bull.*38: 89-97.

[13] Zhang S., Xianting Z., Yongsheng W., Kui C., Wenjian W., (2006), Adhesion strength of sol-gel derived fluoridated hydroxyapatite coatings. Surf Coat Technol. *Surf.Coat.Techno*. 200:6350-6354.

[14] Cheng K., Zhang S., Weng W., (2006), Sol–gel prepared β-TCP/FHA biphasic coatings. *Thin Sol.Films*, 515: 135-140.

[15] Cao M., Wang Y., Guo C., Qi Y., Hu C., (2004),Preparation of ultrahigh-aspect-ratio hydroxyapatite nanofibers in reverse micelles under hydrothermal conditions. *Langmuir*, 20:4784-4786.

[16] Zhang H. G., Zhu Q. S., Wang Y., (2005), Morphologically controlled synthesis of hydroxyapatite with partial substitution of fluorine. *Chem. Mater*. 17: 5824-5830.

[17] Liu J., Li K., Wang H., Zhu M., Xu H., Yan H., (2005), Self-assembly of hydroxyapatite nanostructures by

microwave irradiation, *Nanotechnology*, 16: 82-86.

[18] Peytcheva A., Colfen H., Schnablegger H., Antonietti M., (2002), Calcium phosphate colloids with hierarchical structure controlled by polyaspartates Colloid. *Polym. Sci.,* 280:218-227 .

[19] Beniash E., Simmer J. P., Margolis H. C., (2005), Effects of recombinant mouse amelogenins on the formation and organization of hydroxyapatite crystals in vitro. *J. Struct. Biol*., 149: 182-190.

[20] Chen H., Clarkson B. H., Sun K., Mansfield J.F., (2005), Self-assembly of synthetic structure, *J.Collo.Interf.Sci*. 288: 97-103.