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PREPARATION AND CHARACTERIZATION OF FLUOROHYDROXYAPATITE NANOPOWDERS BY NONALKOXIDE SOL–GEL METHOD

MAJID DARROUDI[a,*], HOSSEIN ESHTIAGH-HOSSEINI[a,b], MOHAMMAD REZA HOUSAINDOKHT[a,b], ABBAS YOUSSEFI[c]
[a] Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, P.O. Box. 91775-1436, Mashhad, Iran
[b] Research Institute of Biotechnology, Ferdowsi University of Mashhad, Mashhad, Iran
[c] Mashhad Glaze Company, Par-e-Tavous Research Institute, Road of Ghouchan, Mashhad, Iran

In this work, Fluorohydroxyapatite (FHA) nanopowders were synthesized using nonalkoxide sol-gel method. Here calcium nitrate tetrahydrate $Ca(NO_3)_2.4H_2O$, phosphorous pentoxide (P_2O_5) and ammonium fluoride (NH_4F) were used to provide Ca-precursor, P- precursor and fluorine reagent, respectively. The FHA powders were calcined at temperatures ranging from 500 to 800ºC. The resultant products have been confirmed to be FHA (apatite phase) using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The thermal stability of FHA powders was studied through diffraction thermal analysis (DTA) and the optimized calcination temperature was found to be 600ºC. The results of transmission electron microscopy (TEM) and Debye-Scherrer equation have shown that the sizes of the FHA particles were in the range of nano-scale.

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Keywords: Sol-Gel, Fluorohydroxyapatite, Nanopowder, X-ray diffraction

1. Introduction

Hydroxyapatite -$Ca_{10}(PO_4)_6(OH)_2$- (HA) material has been clinically applied in many areas of dentistry and orthopaedics because of its excellent osteoconductive and bioactive properties, due to its chemical similarity with the mineral portion of hard tissues [1]. Fluorine ion, which exists in human bone and enamel, can be incorporated into HA crystal structure by substitution of fluorine ions for OH−groups to form Fluoro- Hydroxyapatite (FHA, $Ca_{10}(PO_4)_6(OH)_{2-x}F_x$, where $0<x<2$ is the degree of fluoridation and x=0, pure HA; x=2, pure FA). Incorporation of fluorine into HA, or "fluoridation", reduces its solubility, while maintaining a comparable biocompatibility to that of HA [2]. Many methods, namely, solid-state reaction, wet precipitation and sol–gel processing have been developed for the preparation of FHA powders and ceramics [3-5]. Sol–gel is a wet chemical method that does not need high pH value or high sintering temperature. This method offers a molecular mixing of calcium and phosphorus, which improves the chemical homogeneity of the resulting material. Furthermore, the high reactivity of the sol–gel powders would result in the decrease of calcining and sintering temperature [6]. Many reported sol–gel processes require a strict pH control [7–10].

In this study, we have used Ammonium fluoride (NH_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 [11-13]. Although HPF_6 is a more effective reagent in comparison with NH_4F [14], NH_4F is expected to increase the time of refluxing, thereby improving its effectiveness as a

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[*] Corresponding author: majiddarroudi@gmail.com

good fluorine reagent. Moreover, NH_4F has several other advantages in comparison with HPF_6, which include simplicity and safety at work, easy availability and low cost.

2. Experimental

Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, Merck, GR), phosphorous pentoxide (P_2O_5, Merck, GR) and ammonium fluoride (NH_4F, Aldrich, USA) were selected respectively as Ca-precursor, P-precursor and fluorine reagent. In preparing the solutions, calcium nitrate tetrahydrate was dissolved in absolute ethanol giving rise to a 2 M Ca containing solution; phosphorous pentoxide was dissolved in absolute ethanol to form a 2 M P_2O_5 ethanol solution followed by a refluxing process for 24 h to obtain a clear P-containing solution. A stoichiometry amount of fluorine reagent (x=1; P/F=6) was mixed with P containing ethanol solution to form the P–F mixture. Ca-containing ethanol solution was added drop-wise into the P-F mixture to obtain a Ca /P ratio of 1.67. This mixed solution was refluxed for 32 h to obtain the FHA solution. The FHA solution was dried at 120 ºC for 12 h. The dried powders were divided into four samples and were individually heated at a rate of 2 ºC/min up to respective temperatures of 500, 600, 700 and 800 ºC and then maintained for 15 min at these temperatures. The flow chart of the sol-gel process is illustrated in Fig. 1.

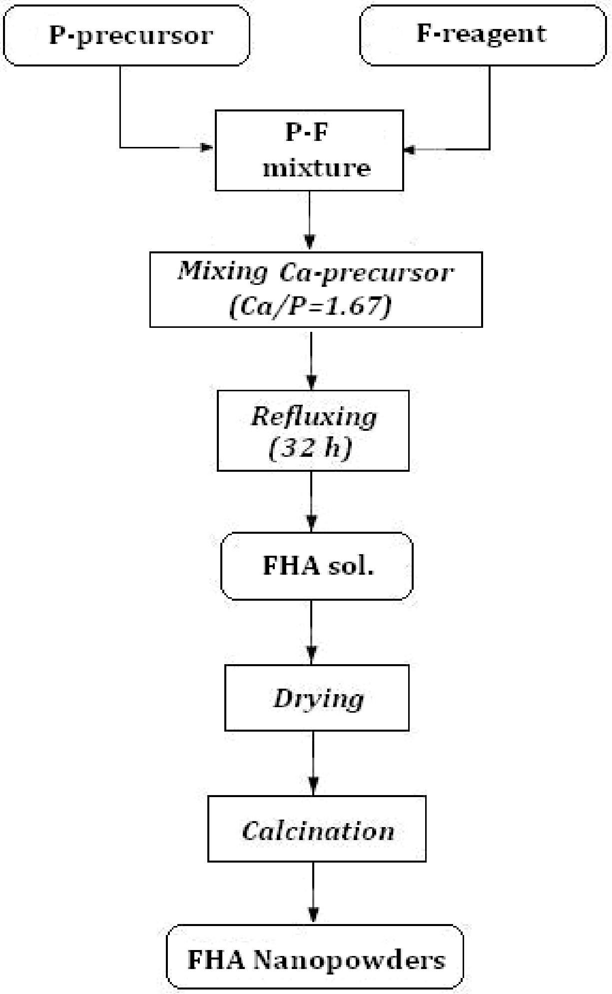

Fig. 1. Flow chart of FHA nanopowders preparation by sol-gel process.

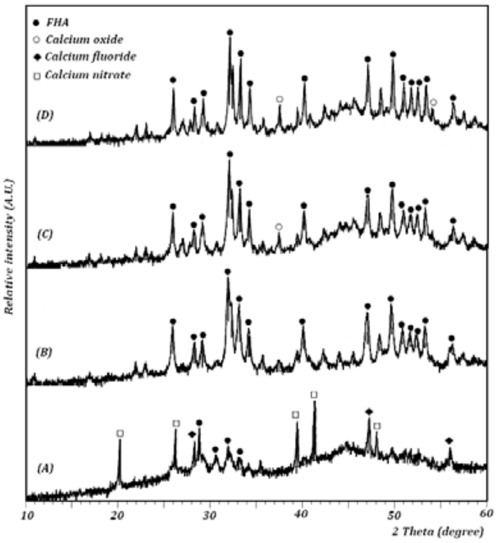

Fig. 2. XRD patterns of the sol-gel-derived FHA powders after heat treatment for 15 min at 500(A), 600(B), 700(C) and 800 ºC (D) in air.

Powders produced were characterized by X-ray diffraction (XRD, Philips, X'pert Pro, Cu Kα, Netherland). The XRD patterns were recorded at a scan speed of 1°/min. The chemical structure of the FHA powder was observed with Fourier transform infrared spectroscopy (FTIR, Nicolet Model 800, USA). The powders were analyzed using differential thermal analysis (DTA, NETZSCH, Germany). Morphological observation of powders was performed in a transition electron microscope (TEM, Leo 912 AB, Germany).

3. Results and discussions

The XRD patterns of the calcined FHA powders at 500, 600, 700 and 800 ºC for 15 min in air are shown in Figs.2. All the powders have similar diffraction profiles. The peaks (002), (211), (112) and (300) are those of the HA structure (JCPDS file card #9-432). For all powders, the main crystalline phase is calcium phosphate (apatite phase) and no obvious impurities such as tricalcium phosphate (α-TCP and β-TCP), calcium oxide (CaO) [15] and calcium fluoride (CaF_2) are found in the XRD patterns. The XRD patterns of products show that with temperature increase after 600 ˚C, there is no change in the intensity of apatite peaks. However no impurity is detected at 600 ˚C only and thus high purity powders are obtained at this temperature.

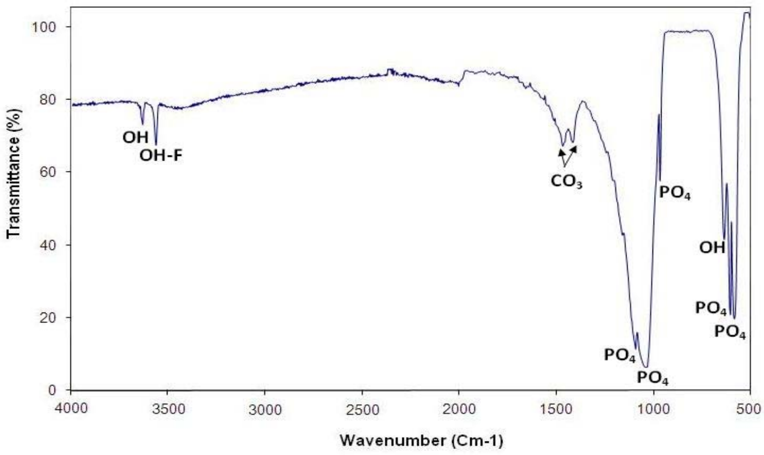

Fig. 3. FTIR spectroscopy of the sol-gel derived FHA after heat treatment at 600 ºC for 15 min in air.

Fig. 3 shows the FTIR spectroscopy of the sol-gel derived FHA after heat treatment at 600 ºC for 15 min in air. The FHA shows the existence of phosphate (PO_4^{3-}) bands at 570(ν_4), 600(ν_4), 960(ν_4), and 1030-1090(ν_3) Cm^{-1}; hydroxyl (OH) bands at 630 and 3570 Cm^{-1}; and OH-F band (stretching) at 3540 Cm^{-1} [16, 17]. Moreover, Carbonate (CO_3^{2-}) bands are observed at 870 and 1360 Cm^{-1}, indicating a substitution of carbonate groups within the apatite structure [16]. The crystal size of the FHA powders is inversely proportional to the peak width according to the Debye-Scherrer equation (eq. 1) [18]:

$$\Delta(2\theta) = \frac{0.9\,\lambda}{D\,Cos(\theta)} \tag{1}$$

where Δ (2θ) represents the peak width at half-maximum intensity of the reflection; λ is the wavelength for CuK_α (λ=0.15418 nm); and D is the crystal size in nanometers. The crystallite sizes are estimated to range from 21.6 to 39.2 nm for the FHA powders calcined from 500 to 800ºC.

Fig.4 shows the DTA curve of the dried FHA powders. The strong endothermic peak at about 100-150ºC indicates evaporation of residual volatiles such as water or ethanol, while the small exothermic peak at about 430-450ºC indicates FHA phase crystallization, and the endothermic peak at about 550-570ºC is the result of FHA phase formation. However, for the FHA, no appreciable change in DTA curve is observed in high temperature region (600-800ºC), indicating formation of a stable FHA phase. The nanocrystalline structure of the FHA powders is confirmed by TEM. Fig. 5 shows representative TEM images recorded on copper grid with holly carbon film at different magnifications from the FHA powders. These are in good agreement with the particle size measurements obtained using XRD patterns through Scherrer equation.

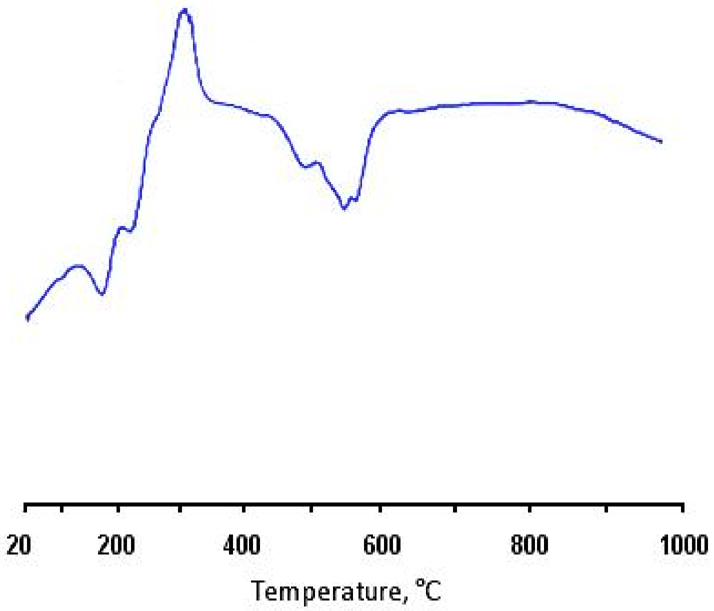

Fig. 4. Differential thermal analysis (DTA) curve of the dried FHA powders.

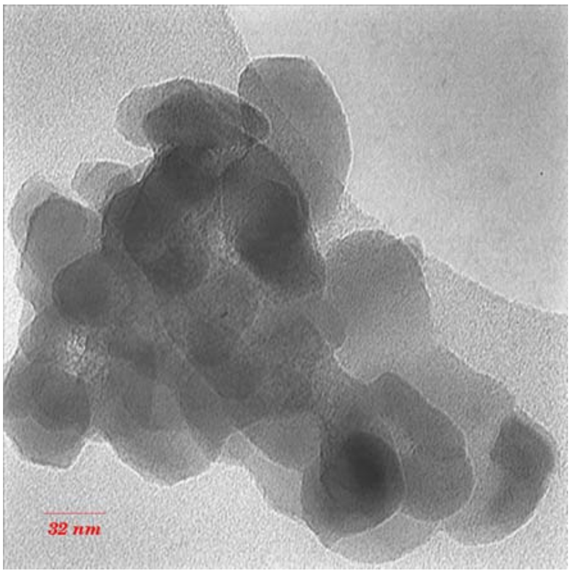

Fig. 5. TEM image of the calcined FHA powders at 600˚C for 15 min in air.

4. Conclusions

In this study, FHA has been synthesized with NH_4F as the fluorine containing reagent using nonalkoxide sol-gel method. XRD measurements showed that the apatite phase has existed in FHA powders without impurity at 600°C. The sizes of FHA particles were estimated by Debye-Scherrer equation and the TEM results also showed that the sizes of the FHA particles were in the range of nano-scale.

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