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Crystal growth and structural analysis of hydroxyapatite nanofibers synthesized by the hydrothermal microwave-assisted method

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ABSTRACT

Hydroxyapatite nanofibers were synthesized by the hydrothermal microwave-assisted method at 170 °C using a mixture of $CaNO_3$, KOH, K_2HPO_4 and glutamic acid as precursors. The reaction took place inside of pressurized Teflon vessels at 80 bars. The reaction time was varied from 15 up to 45 min meanwhile temperature, microwave power and precursor composition were kept constant. Crystal phase composition, functional groups, vibrational modes, surface morphology and nanostructure were studied by X-ray diffraction, Fourier transform infrared spectroscopy, Raman spectroscopy, Scanning Electron Microscopy and High Resolution Transmission Electron Microscopy, respectively. Hydroxyapatite nanofibers, with diameters in the order of nanometers and lengths of micrometers, were obtained; their surface seems to be smooth with well-defined shapes and edges. The length increased as the reaction time, so fibers as long as 70 μm were obtained with a diameter the order of 450 nm. According to the XRD patterns, preferential crystalline orientations in the [211] and [300] directions were observed, which are attributed to the glutamic acid concentration used in the reacting mixture as well as to the reaction time. SEM images showed a hexagonal needle-like morphology of nanofibers and studies by TEM and HRTEM indicate that those nanofibers grow in a preferential crystalline direction along the "c" axis of the HAp structure.

1. Introduction

Hydroxyapatite is the major constituent of the bones in vertebrates, representing 69% of weight, on the average [1]. Synthetic hydroxyapatite is of great interest because it possesses similarity with the structure of natural bone, so it is a material with a high biocompatibility [2]. Recent studies on the regeneration of bones have revealed the formation of hierarchical structures in the process of bio-mineralization; these structures are basically formed by hydroxyapatite nanocrystals with different morphologies. Various methods have been used for the synthesis of hydroxyapatite nanostructures, among them: hydrothermal [3], electrospinning [4], chemical precipitation [5] and microwave irradiation [6]. The main characteristic of these processes is the possibility to control the morphology and dimensions of nanostructures by adjusting the experimental parameters, such as microwave power, pressure, temperature, reaction time and precursor composition [7]. Recently, it was found that by adding some chemicals to the precursor, as glutamic acid, it is possible to modify the morphology of the hydroxyapatite nanostructures. Depending on the concentration of glutamic acid in the precursor, the hydroxyapatite nanostructures can form nanoplates, nanowires, nanofibers and nanoparticles [8]. In the field of applications, the control of morphology is of great importance, over all if we are looking for applications in the area of biomaterials. On the other hand, the production of synthetic hydroxyapatite at industrial scale requires a long time for synthesis process [9]. In this way, the microwave irradiation is the most efficient method to grow hydroxyapatite because the duration of a synthesis process can be reduced drastically to less than the fourth part, respect to the other methods

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[10–13], some of the most relevant advantages of this method are that the energy transfer, as well as the reactions, are faster and direct than in other methods and purer compounds can be obtained, and also, the reaction parameters can be optimized and controlled.

Several investigations have reported that with the process of microwave-assisted synthesis, HAp nanostructures have been obtained with high purity [11–13]. Lak et al. reported the synthesis of nanorods of hydroxyapatite via microwave irradiation, however their nanostructures present poor crystallinity with acceptable morphology [14]. Liu et al. reported hydroxyapatite needle-like nanostructures with poor crystallinity and also the morphology is not well controlled [15].

On other hand, the use of pressurized quartz vessels in combination with microwave heating helps to maintain homogeneous temperature and pressure in the reaction mixture, enabling an easier and faster growth of the HAp nanostructures. It is noteworthy that within the working group has been reported research in which it has been possible to obtain HAp nanostructures with high crystallinity and a well-controlled morphology [16]. In this previous work, the glutamic acid concentration was varied in the reacting mixture, in order to evaluate its influence on the morphology of HAp nanostructures. Nanoparticles, nanoplates and nanofibers were mainly obtained and their crystal structure was analyzed. Now in this work, the goal was the obtaining of hydroxyapatite nanofibers with a high crystallinity and with a preferential crystalline orientation. The reaction time was varied to evaluate its influence on the crystal orientation, crystallite size and the dimensions of fibers. Additionally, the synthesis procedure was optimized to synthesize nanofibers in a reproducible way.

2. Materials and methods

2.1. Synthesis of HAp nanostructures

The growth of the nanofibers was carried out using the synthesis procedure described in a previous work [16]. The microwave assisted hydrothermal method was performed using a microwave oven Synthos 3000 by Anton Paar. The reaction conditions consist of a power of 1200 W a pressure of 80 bars and temperature of 170 °C. The precursors were prepared from two aqueous solutions, in the first one: 4 g of glutamic acid was mixed with 1.14 g of calcium nitrate and mixed in 200 ml of distilled water, with stirring for 2 h at 60 °C. In the second one: 0.97 g of potassium phosphate was mixed with 0.70 g of potassium hydroxide and then poured in 200 ml of distilled water and stirred for 15 min. Finally, both solutions were mixed for 10 min to obtain the reacting mixture. In the next step, 50 ml of the reacting mixture were placed in a quartz tube, using a total of eight tubes in each synthesis reaction (400 ml of reacting mixture), and then all tubes were introduced into the microwave oven. When the reaction time was over, the solution of each tube was recovered and filtered to obtain hydroxyapatite powders.

In all synthesis reaction, the chemical composition, the power and temperature in the microwave oven were kept constant; only the reaction time was varied in order to analyze its effects on the morphology, dimensions and crystal structure of the HAp nanostructures obtained. The experimental conditions of these synthesis reactions are shown in Table 1.

Table 1
Experimental conditions in the synthesis reactions made in this work.

Sample	Temperature (°C)	Power (Watts)	Reaction time (minutes)
HAp-1	170	1200	15
HAp-2	170	1200	30
HAp-3	170	1200	45

2.2. Characterization of HAp nanostructures

2.2.1. Phase composition: XRD

X-ray powder diffraction was used to identify the crystalline phases contained in all samples, so as to determine any potential preferential crystalline orientation produced by the variation of reaction parameters. Powder samples were densely packed in an aluminum holder without any milling process. Wide angle X-ray experiments were carried out in a Rigaku Ultima IV diffractometer using the Cu k_α radiation ($\lambda = 1.5406$Å), an accelerating voltage of 40 kV and a current of 30 mA. Diffractograms were recorded with a Solid State D/teX-ULTRA Detector from 5 through 80° on a 2θ scale with a rate of 10° per minute. Spectrum analysis software, MDI Jade V 5.0.37, was used.

2.2.2. Functional groups: FTIR

In order to identify the HAp molecule through its functional groups and to determine its purity, a FTIR spectrometer Bruker model Vector 33 was used. The Infrared spectra were recorded in Medium Infrared (MIR) between 650 and 4000 cm^{-1} with a resolution of 1 cm^{-1}. Each sample was mixed with KBr (potassium bromide) in a ratio of 3:1, the powders were ground to form a homogeneous mixture.

2.2.3. Vibrational modes: Raman spectroscopy

To analyze the vibrational modes in the HAp samples, a Raman spectrometer Bruker model Senterra was used. The operation condition were a voltage of 100 mV, a resolution of 3-5 cm^{-1} and a 20X objective. Samples were placed in powder.

2.2.4. Morphology and microstructure: SEM

Morphological, topological and microstructural analyses of all samples were carried out in a JEOL JSM 6060LV Scanning Electron Microscope. The analysis was performed using 20 kV electron acceleration voltage and the images were formed by secondary electrons. All samples were placed on copper sample holders and covered with a gold thin film done by sputtering to avoid the electrostatic charge accumulation.

2.2.5. Microstructure: TEM and HRTEM

In order to analyze with detail the morphology and crystalline structure of HAp nanostructures, a Transmission Electron Microscopy was performed using a JEOL JEM 2010HT with a resolution of 0.19 nm. In all observations an accelerating voltage of 200 kV was used and high resolution images were recorder. Selected area electron diffraction was performed; TEM and high resolution images were analyzed through the Digital Micrograph software provided by Gatan. Interplanar distances were determined and Fast Fourier transforms were generated to analyze the crystalline structure of HAp. Samples were prepared by dispersing a fraction in ethanol and depositing a drop of this dispersion onto carbon coated of 3 mm Cu grids.

2.2.6. Elemental composition

EDS. In order to obtain the elemental composition of nanofibers, Electronic Microprobe for Microanalysis (EPMA) JXA -8530F was used. The operation conditions were: A voltage of 10 kV and a current of 0.10 nA. A small tablet was made with each sample and then it was coated with a graphite thin film.

3. Results and discussion

3.1. Structural characterization

3.1.1. Crystalline phases

The x-ray diffraction is an excellent technique to identify the crystalline components in a sample and to analyze the crystal structure of a particular constituent. Fig. 1a) shows the recorded diffraction patterns of the three HAp samples showing the effect of the reaction

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