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The effect of ultrasonic irradiation on the crystallinity of nano-hydroxyapatite produced via the wet chemical method

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ABSTRACT

Nanohydroxyapatite (nHAp) powders were produced via aqueous precipitation by adopting four different experimental conditions, assisted or non-assisted by ultrasound irradiation (UI). The nHAp powders were characterized by X-ray diffraction, energy-dispersive X-ray fluorescence, Raman and attenuated total reflection Fourier transform infrared spectroscopies, which showed typical surface chemical compositions of nHAp. Analysis found strong connections between UI and the crystallization process, crystal growth properties, as well as correlations between calcination and substitution reactions.

1. Introduction

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) is used as a biomaterial for the regeneration of bone tissue because of its chemical and crystallographic similarity to the main inorganic component of natural bone [1,2].

The close chemical similarity of HAp to natural bone has driven extensive research efforts to use synthetic HAp as a bone substitute and/or replacement in biomedical applications [3,4]. To date, many methods have been developed to prepare HAp powders. The techniques include: sol–gel [5], homogeneous precipitation [6], hydrothermal [7], mechano-chemical [8], RF plasma spray [9], spray dry [10], combustion synthesis [11,12], ultrasonic spray freeze-drying [13], sonochemical synthesis [14] methods, etc. In general, the "wet chemical process", is usually used to prepare HAp powders because it is simple and does not require expensive equipment.

HAp is classified as one of the best biocompatible and bioactive materials for many biological applications such as bone repair scaffolds [15]. Recent advances in biomaterial research have suggested that the best osteocompatibility of HAp could be achieved if the structure, size, and morphology of the crystal were closer to that of biological apatite. As a result, nano-hydroxyapatite (nHAp) is of great interest [16].

For specific biomedical applications, it is necessary to produce nHAp crystallites with either reduced particle-size and high surface areas, or controlled morphology, or both. Current studies investigate different routes to synthesize nHAp powders [17–19] in order to achieve a bioactive phase that can be used in combination with other materials that lack this property [20] and, thus, produce nanostructured composite materials.

Recent studies have shown that the reactivity of chemical species in solution, involved in a synthesis process can be stimulated by ultrasonic irradiation (UI) of the reaction mixture. This type of treatment causes cavitation in an aqueous medium inducing formation, growth, and collapse of micro-bubbles. This intense agitation process provokes the dissolution–precipitation of solids which reduces particle size and surface activation of the product [21–23]. Although the efficiency of the synthesis process depends on many variables, the type of ultrasonic agitation device is the principal factor; for example, the use of a tip ultrasonic homogenizer is more efficient than an ultrasonic bath.

In this work, nHAp was produced using an aqueous precipitation process, comparing four different experimental conditions, assisted or non-assisted by ultrasound irradiation, to identify which resulted in the smallest particle-size and was the most similar to the nHAp of bone tissue.

2. Materials and methods

2.1. nHAp precipitation

The precipitations were done under four different conditions. The solutions used for all of the samples were as follows: 100 mL of 0.167 M of $Ca(NO_3)_2.4H_20$ and 100 mL of 0.1 M of $(NH_4)H_2PO_4$. NH_4OH was added to both solutions to fix the pH ~10. These initial proportions yield theoretical calcium to phosphorous ratio (Ca/P) of 1.67. These details are summarized in Fig. 1.

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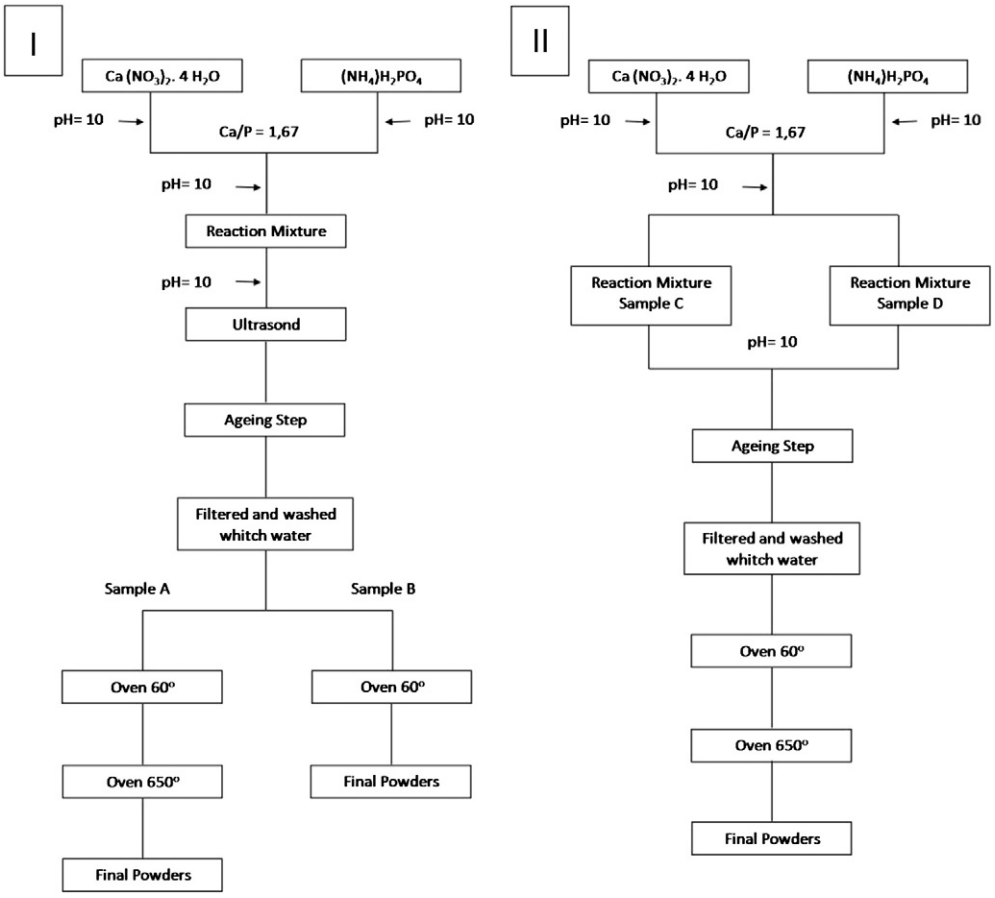

Fig. 1. Flowchart I shows the parameters for samples A and B, with the effect of Ultrasound. Flowchart II shows from left to right the parameters without the ultrasound irradiation, described as samples C and D, respectively.

For samples A and B, the solutions were mixed by pouring one solution into the other. Thereafter, the precipitations were subjected to ultrasound irradiation (UI) for 30 min (Ultrasonic Processor 500 W; 20 kHz; 13 mm probe; model: SO-VCX-500, SONICS), maintaining the pH above 10 every 10 min. The resulting suspensions were left to age for 120 h. After the samples were filtered and washed with water, they were subsequently left to dry at 60 °C for 4 h. Afterwards, only sample B was calcinated at 650 °C for 1 h.

Samples C and D were made without UI process. For sample C, the solutions were mixed by pouring one solution into the other, and left for 1 h on a heating plate at a temperature of 60 °C. For sample D, the ammonium phosphate solution was stirred constantly and kept at 60 °C while adding the solution of $Ca(NO_3)_2.4H_2O$ using a slow drip at a rate of 1.2 mL/min. Both resulting precipitate suspensions were aged for 120 h, and after filtered and washed with water, both were calcinated at 650 °C for 1 h.

The summary of these samples produced were show in Table 1.

Table 1
Wet chemical method parameters.

Samples	Wet chemical method	Thermal treatment (°C)
A	Ultrasound irradiation	60
B	Ultrasound irradiation	650
C	Mixture	650
D	Dropwise	650

2.2. Characterization of HAp nanopowders

The phase and crystallinity of the resulting nanopowders were characterized by X-ray diffraction (XRD: Lab X (XRD-6000)), Shimadzu. X-ray diffractometer with monochromatic CuKα radiation generated at 40 kV and 50 mA. The data were collected for 40 min, over a range of angles from 20 to 80° with a scanning step of 0.02°. To quantify the crystallinity and to calculate the crystallite size, only the data from 24 to 36° were used. The nHAp preferential growth plane was calculated using the equation suggested by Hu et al. [24].

The crystallinity can be evaluated using the following empirical relation (Eq. (1)) [25]:

$$XC = 1 - \left(V_{112/300}/I_{300}\right) \quad (1)$$

where XC is the crystallinity, I_{300} is the intensity of the (300) reflection, and $V_{112/300}$ is the intensity of the hollow between (112) and (300) reflections, which completely disappear in non-crystalline samples.

The crystallite size in the [002] direction can be estimated from the peak broadening of XRD reflection according to the Scherrer formula [26] (Eq. (2)):

$$r = K\lambda/B \times \cos\theta \quad (2)$$

where r is the crystallite size [nm], K is a constant taken as 0.9, k is the wavelength of monochromatic X-ray beam [nm] ($\lambda_{CuK\alpha} = 0.15418$ nm), B is the width of the peak at half-intensity (FWHM) of (002) reflection