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Sonochemical Synthesis of Hydroxyapatite Nanoparticles with Different Precursor Reagents

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Different precursor chemicals ($3Ca(OH)_2$, $Ca(NO_3)_2$ and CaO as Ca^{2+} sources, H_3PO_4 and $(NH_4)_2HPO_4$ as PO_4^{3-} sources were used to synthesis of nanosized hydroxyapatite powder with ultrasonic precipitation method. The effect of different chemical precursors was investigated. Sample characterization was achieved by powder X-ray diffraction, the Fourier transformed infrared transmission spectroscopy, zeta sizer, scanning electron microscopy, density and surface area measurements.

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1. Introduction

The use of bone-substituted materials in the science of biomaterials is an important objective due to their bioactive and biocompatible properties [1]. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA) is the major constituent of human bone. Due to its good biocompatibility and osteoconductivity, synthetic HA has been widely used as bone graft substitutes, drug delivery devices, and in purification of proteins [2]. Therefore calcium phosphates have been used in an interdisciplinary field of science involving chemistry, biology, medicine, dentistry and geology for over 20 years [1]. The natural bone is a composite mainly consisting of nanosized, needle-like HA crystals (accounts for about 65 wt% of bone) and collagen fibers. Scientists have been focused on producing nanosized high quality HA bioceramics for artificial bone substitution [1].

Hydroxyapatite can be synthesized by various methods including sol–gel, homogeneous precipitation, hydrothermal, mechano-chemical, RF plasma spray, spray drying, combustion synthesis, supersonic rectangular jet impingement and precipitation method [3]. The precipitation method is the most studied method for producing HA powders. This method is economic and simple to apply in industrial conditions. In general, produced HA powder particles have low quality with a large particle size, wide particle size distribution and agglomerates. Ultrasonication is an effective way of breaking up aggregates and of reducing the size of nanoparticles. It has been well recognized that the ultrasonic irradiation caused cavitation in an aqueous medium where the formation, growth and collapse of microbubbles occurred. This can stimulate the reactivity of chemical species involved, resulting in the acceleration of the heterogeneous reactions between liquid and solid reactants effectively. These processes, involving dissolution and precipitation of solids through particle size reduction and surface activation by intensive stirring, have been also identified [4]. For crystallization of HA, increasing the power decreases the particle size until 300 W power but no HA crystals form above this power. Therefore, the particle size of the crystal can be controlled through the ultrasonic power applied. With large kinetic energies and speeds, the solute molecules will have an increased opportunity to collide with each other and hence insert themselves into the crystal lattice more uniformly and easily [5]. Thus we chose 300 W ultrasonic power for nanosized hydroxyapatite synthesis in this study.

In literature [1, 6–11] ultrasonic precipitation method has been reported many times with theoretical Ca/P ratio of 1.67. In this study, ultrasonic irradiation is applied with an ultrasonic bath device to produce nanosized HA powder. Also the theoretical Ca/P ratio of HA is chosen to be close to 1.67. Apart from the other reported studies, different chemical precursors ($Ca(OH)_2$, $Ca(NO_3)_2$, and CaO as Ca^{2+} sources; H_3PO_4 and $(NH_4)_2HPO_4$ as PO_4^{3-} sources) were used as Ca^{2+} and PO_4^{3-} sources to see the most suitable ones for pure nanosized hydroxyapatite powder synthesis.

2. Experimental method

HA powders were prepared by wet chemical precipitation method using different chemical precursors. Experimental flow diagram of HA synthesis is given in Fig. 1. All the chemicals were analytical grade ($Ca(OH)_2$, H_3PO_4, $Ca(NO_3)_2$; Merck-96%, $(NH_4)_2HPO_4$; Merck-99% and CaO) were selected in this work. Ca^{2+} ion precursors and PO_4^{3-} ion precursors were weighted at molar ratio of Ca/P=1.67 and dissolved with 100 ml distilled water in different vessels to prepare homogeneous solutions. About 100 ml PO_4^{3-} ion precursor suspension was poured into the 100 ml of Ca^{2+} ion precursor suspension

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slowly while it was being irradiated with ultrasonic bath device (Bandelin Sonorex, Germany) which has a stirring frequency of 35 kHz and 160–320 W power to get a homogeneous reaction.

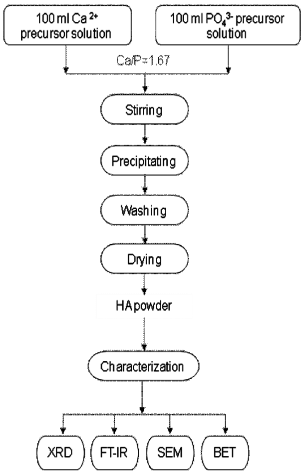

Fig. 1. Experimental flow diagram of HA synthesis.

The reactions according to the precursor type is indicated as in the following:

1. $Ca(OH)_2$ and H_3PO_4 precursors: U1 sample

$$3Ca(OH)_2 + 3H_3PO_4 \rightarrow 3CaHPO_4 + 6H_2O\,, \tag{1.1}$$

$$5Ca(OH)_2 + 3H_3PO_4 \rightarrow \tfrac{1}{2}\,Ca_{10}(PO_4)_6(OH)_2 + 9H_2O\,, \tag{1.2}$$

$$2Ca(OH)_2 + 3CaHPO_4 + 6H_2O \rightarrow \tfrac{1}{2}\,Ca_{10}(PO_4)_6(OH)_2 + 9H_2O\,. \tag{1.3}$$

2. $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ precursors: U2 sample

$$10Ca(NO_3)_2 + 6(NH_4)_2HPO_4 + 2H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 12NH_4NO_3 + 8HNO_3\,. \tag{2.1}$$

3. CaO and H_3PO_4 precursors: U3 sample

$$3CaO + 3H_2O \rightarrow 3Ca(OH)_2\,, \tag{3.1}$$

$$3Ca(OH)_2 + 3H_3PO_4 \rightarrow 3CaHPO_4 + 6H_2O\,, \tag{3.2}$$

$$5Ca(OH)_2 + 3H_3PO_4 \rightarrow \tfrac{1}{2}\,Ca_{10}(PO_4)_6(OH)_2 + 9H_2O\,, \tag{3.3}$$

$$2Ca(OH)_2 + 3CaHPO_4 + 6H_2O \rightarrow \tfrac{1}{2}\,Ca_{10}(PO_4)_6(OH)_2 + 9H_2O\,. \tag{3.4}$$

Resulting solution was stirred for one hour at room temperature and then left to precipitation. The wet cake was washed with distilled water three times. Then the powder was dried in an oven at 37 °C. The same operations were repeated for another precursor system using ultrasonic bath.

3. Results and discussion

The HA powders were analysed by X-ray diffraction (XRD, Philips X-ray diffractometer). The chemical nature and molecular bond structure of the synthesized HA powders were determined by using the Fourier transform infrared (FTIR) technique (Perkin-Elmer Spectrum One B V 5,01). Particle size distribution of the powders were measured by a zeta sizer (ZS ZEN 3600, UK). The specific surface area of the resulting powders were measured by a Brunauer–Emmett–Teller (BET) technique (Autosorb-1, Quantachrome Co., USA), using N_2 as an adsorption gas.

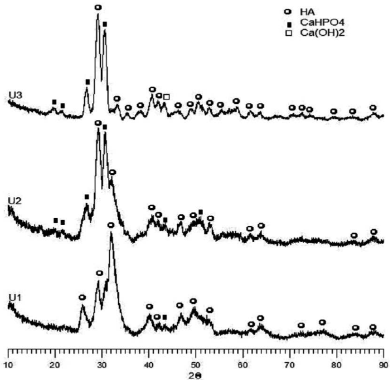

Fig. 2. XRD spectra of U1, U2 and U3 powders.

In Fig. 2, the XRD patterns showed very strong formation of HA phase for U1 sample while there are $Ca(OH)_2$ and $CaHPO_4$ secondary phases in the U2 and U3 powders.

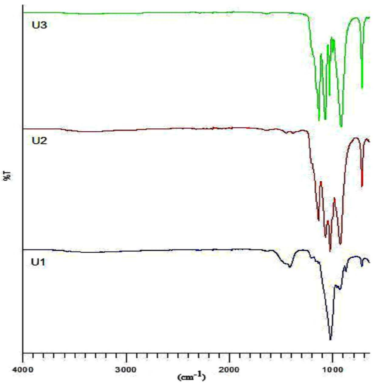

Fig. 3. FTIR spectra of U1, U2 and U3 powders.

Figure 3 exhibits FTIR spectrum of the U1, U2 and U3 powders. In the spectrum of U1 powder, the band at 1415 cm^{-1} belongs to OH^- bonds and the typical bands at 1032, 932 and 873 cm^{-1} belong to PO_4^{3-} groups in the material [10]. The peaks exist between 1139 and 650 cm^{-1} which shows the formation of PO_4^{3-} groups [8]. Functional groups exist between 1500 and 3600 cm^{-1}. On the other hand, the region between 1500 cm and 400 cm^{-1} is named finger print region. Because this interval shows the vibrations of the whole molecule and it is used to compare two samples to determine the similarity or difference. When the FTIR spectra of three samples are compared, it can be observed that they have the same chemical content. Similarly, U2 and U3 powders have the same contents as well.

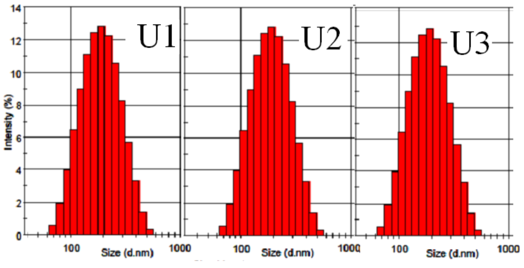

Fig. 4. Particle size distribution of U1, U2 and U3 samples.

Particle size distributions investigation results of size distribution analysis were given in Fig. 4. The minimum particle size of U1, U2 and U3 samples were 68 nm, 79 nm, and 91 nm, respectively.

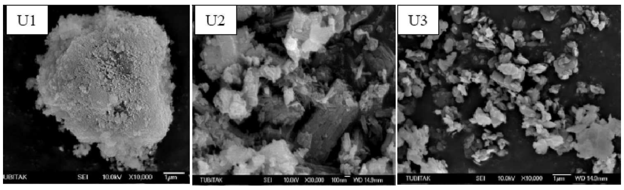

Fig. 5. SEM micrographs of U1, U2 and U3 powders.

In Fig. 5 SEM micrographs exhibit different powder morphologies. U1 powder that was synthesized with $Ca(OH)_2$ and H_3PO_4 precursor chemicals has a spherical shape. However the powder which was synthesized with $Ca(OH)_2$ and H_3PO_4 precursor chemicals has rod like particles and U3 powder that was synthesized with CaO and H_3PO_4 has an elliptic particle morphology.

BET results give an important clue about the particle sizes of synthesized powders. As a result of multipoint BET analysis, U3 sample which was synthesized with CaO and H_3PO_4 precursors has the lowest total surface area as given in Table below.

TABLE

BET and density analysis results of U1, U2 and U3 samples.

Sample	BET [m^2/g]	Density [g/cm^3]
U1	37.20	3.52
U2	21.50	3.40
U3	9.86	3.38

4. Conclusion

Particle size measurement results of U1, U2 and U3 HA powders are given in Fig. 4. The particle size values are in good agreement with SEM and surface area measurement results. U1 sample has lowest particle size and highest surface area with a spherical morphology.

Acknowledgments

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