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Procedia Engineering 42 (2012) 1816 – 1821

Procedia Engineering

www.elsevier.com/locate/procedia

20th International Congress of Chemical and Process Engineering CHISA 2012
25 – 29 August 2012, Prague, Czech Republic

Synthesis of sphere-like nanoparticles of hydroxyapatite

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Abstract

Hydroxyapatite due to its excellent biocompatibility, bioactivity and osteoconductivity is widely used in orthopedic, dental, and maxillofacial applications for bone reconstruction. Nanoparticles of hydroxyapatite, which are prepared synthetically, have chemical and structural similarity with nature hydroxyapatite of bones and teeth. Sphere-like nanoparticles of hydroxyapatite were synthesized by wet chemical precipitation method under atmospheric pressure, using calcium nitrate and diammonium phosphate as reactants and ammonia was chosen as pH adjusting agent. The crystal morphology and particle size were analyzed by atomic force microscopy and X-ray disc centrifuge system. Composition and chemical structure were identified by X-ray diffraction, Fourier transform infrared spectroscopy and thermogravimetric analysis.

Keywords: Nanoparticles; hydroxyapatite; biomedical application

1. Introduction

The natural bone is a composite mainly consisted of nano-sized hydroxyapatite crystals well arranged within the polymeric matrix of collagen type I. The mineral part of human bone is especially made of nano-sized carbonated hydroxyapatite crystals, which represent 65 % of its total weight [1].

Synthetic nano-hydroxyapatite (n-HAp) is known to be one of the most important implantable materials because of its biocompatibility, bioactivity and osteoconductivity coming from the analogy to

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doi:10.1016/j.proeng.2012.07.576

the mineral components of natural bones that is why it is used as a substitute material for human hard tissues. Hydroxyapatite has attracted much attention as a material for orthopedic, dental and maxillofacial applications for bone reconstruction [2, 3]. Synthetic n-HAp exhibits strong affinity to host hard tissues due to the chemical similarity between n-HAp and mineralized bone of human tissue. The recent trend in bioceramic research is focused on improving mechanical and biological properties of hydroxyapatite using nanotechnology because of poor mechanical properties [4].

2. Experiment

Nanoparticles of hydroxyapatite were prepared by wet chemical precipitation method. 0.3 M water solution of calcium nitrate ($Ca(NO_3)_2.4H_2O$, Penta, Czech Republic) and 0.3 M water solution of diammonium phosphate ($(NH_4)_2HPO_4$, Lachema, Czech Republic) were used as initial solutions. Solution of $(NH_4)_2HPO_4$ was added drop by drop in solution of $Ca(NO_3)_2$ under vigorous stirring at 40 °C. Ammonia was used for adjustment of pH value. Suspension was stirred 1.5 h after addition of initial solution. The resultant suspension was filtered and washed with distilled water to remove the residual impurities. The final product was atmospherically dried at room temperature.

The crystal morphology and particle size were analyzed by atomic force microscopy (AFM, Scanning Peak Microscopy, Dimension Icon, Bruker, Germany) under ambient conditions by mode Peak Force QNM (Quantitative NanoMechanics). The silicon nitrid probe having a resonant frequency 45-95 kHz, a force constant 0.4 N/m and a radius of curvature 2 nm was used.

Particle size was studied by X-ray disc centrifuge system (BI-XDC Particle Sizer, Brookhaven Instruments Corporation, USA), speed of disc rotation was 600 rpm. The XRD pattern was recorded using X-ray diffraction (D8 ADVANCE Diffractometer, Bruker AXS, Germany) with CuK_α radiation (λ = 1.5418 Å). The sample was further characterized by Fourier transform infrared spectroscopy (FTIR Spectroscope Nicolet IMPACT 400D, USA) in the range of 400-4000 cm^{-1} using KBr pellet technique. Thermogravimetric analysis (TGA Q500, TA Instruments, USA) of the material was performed between 25-900 °C in air at a heating rate of 10 °C per minutes.

3. Results and discussion

The AFM images of n-HAp are shown in Fig.1 and Fig. 2. The size of hydroxyapatite crystal was nano-grade. The sphere-like primary crystals of n-HAp were 30-50 nm in diameter and some aggregates could be observed.

XDC method was used for measurement of particle size. This method measures sedimentation of nanoparticles in a gravitational or a centrifugal field. X-rays from a low power X-ray tube are passed through the disc. The intensity of the transmitted beam is measured with a detector consisting of a scintillation counter whose output is recorded by the computer as a function of time. Curve of particle size distribution can be observed in Fig.3. Determined n-HAp particle size distribution was 240-410 nm. It is evident difference between results from AFM and XDC methods. XDC showed bigger size of nanoparticles because of possible formation of aggregates.

XRD diffractogram (Fig. 4) confirmed hexagonal structure of hydroxyapatite with P63/m space group and cell dimensions of a = b = 9.43 Å; c = 6.88. Å.

FTIR analysis, which is shown in Fig. 5, displayed specific vibrations for bands present in hydroxyapatite crystals. Phosphate groups were detected at 960 cm^{-1}, 1033 cm^{-1}, 575 cm^{-1} and 601 cm^{-1}; OH- band was identified at 3575 cm^{-1} inside the H_2O region. Furthermore, carbonate bands were observed at 1425 cm^{-1} and 875 cm^{-1}. X-ray diffraction and infrared spectroscopy confirmed structure of hydroxyapatite. These carbonate substitutions of hydroxyl or phosphate groups appeared during wet

chemical precipitation because of ambient carbon dioxide solubilization related to vigorous stirring. This modification of stoichiometric n-HAp is similar to natural n-HAp in bones.

TGA analysis showed 8.5 % loss of weight, which was a result of removal of adsorbed and possible lattice water, decarboxylation of HAp or condensation of HPO_4^{2-} releasing water, as can be seen from Fig. 6.

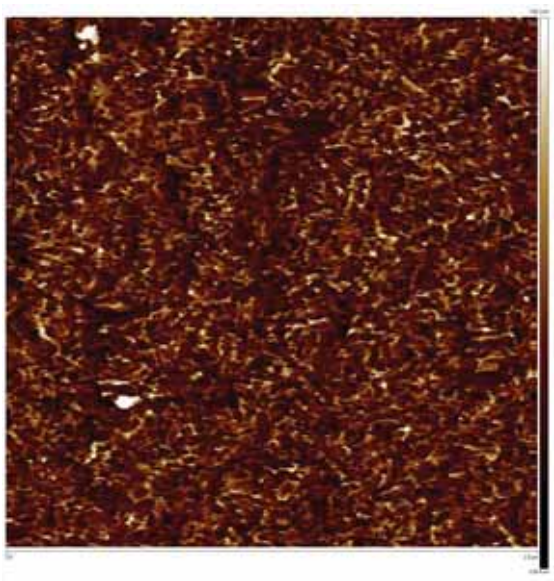

Fig. 1. AFM image of n-HAp on mica, primary nanoparticles 30-50 nm, map of adhesion, scan 2 μm

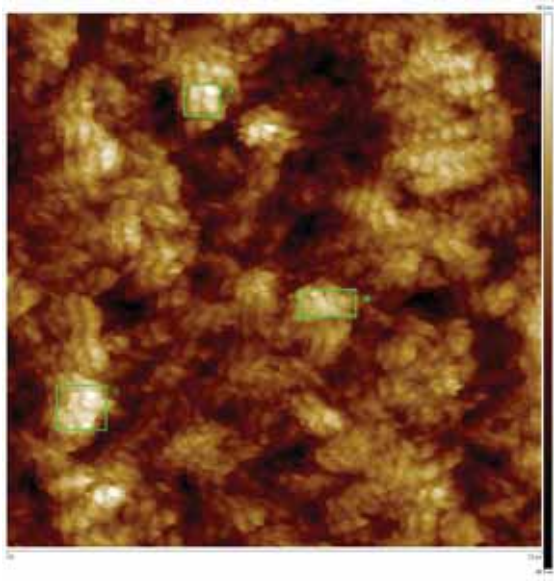

Fig. 2. AFM image of n-HAp on mica, aggregates (A: 140x120 nm, B: 214x100 nm, C: 190x170 nm), topography, scan 2 μm

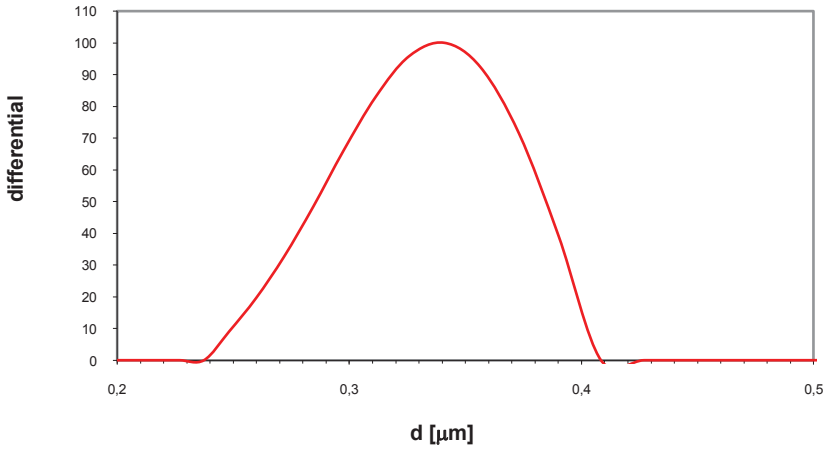

Fig. 3. Particle size distribution of sphere-like nanoparticles

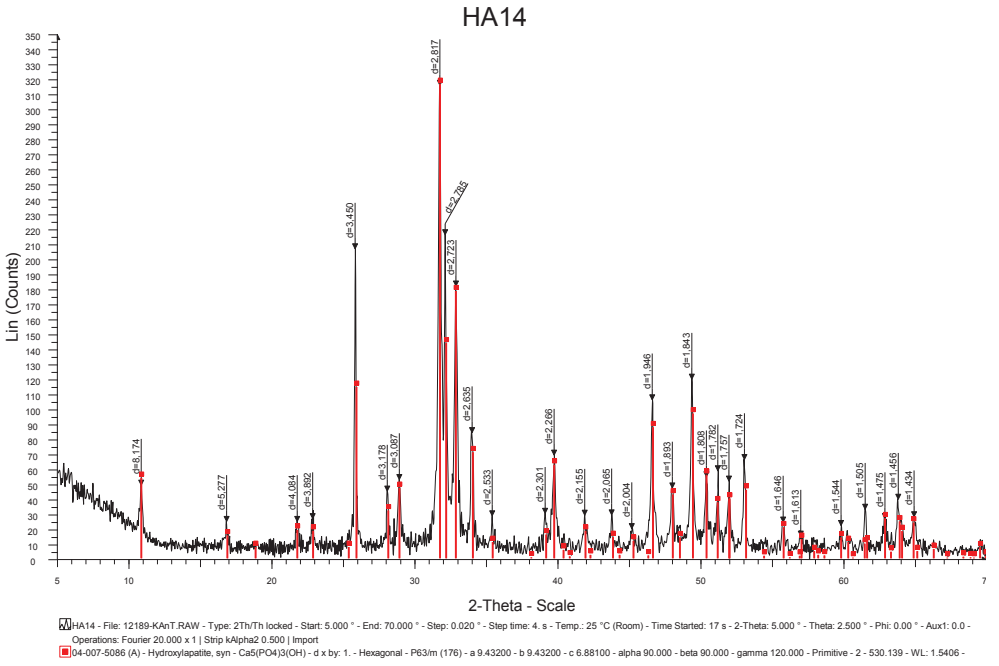

Fig. 4. X-ray diffraction of powder of n-HAp

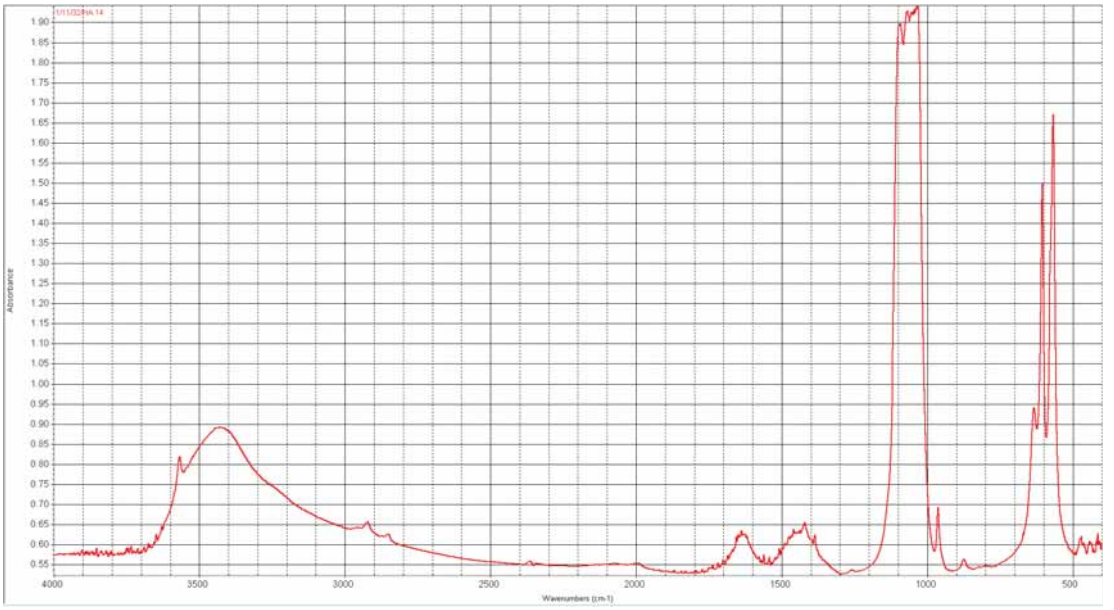

Fig. 5. FTIR spectrum of n-HAp

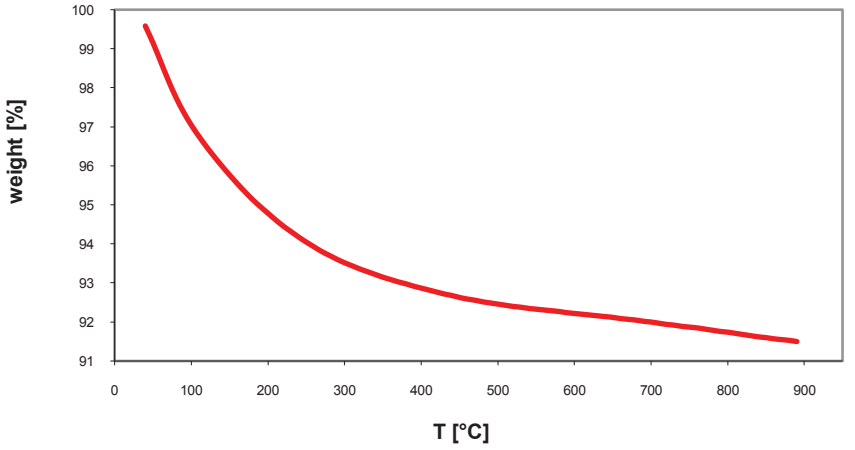

Fig. 6. TGA analysis of nano-powder of HAp

4. Conclusions

This work was focused on preparing sphere-like nanoparticles of hydroxyapatite. Nanoparticles were successfully prepared via wet chemical precipitation method using calcium nitrate tetrahydrate and diammonium phosphate as precursors. Shape, size and chemical structure of nano-hydroxyapatite ware

studied. AFM showed that the primary particles have spherical shape and diameter 30-50 nm. FTIR spectra and XRD diffractogram confirmed structure of hydroxyapatite.

Acknowledgements

This work was supported by IGA University of Pardubice in terms of project SG FChT04.

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