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Comparative Study of Sonochemical Synthesized ß-TCP- and BCP-Nanoparticles

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Abstract. Hydroxyapatite (HA), beta tricalcium phosphate (ß-TCP) and biphasic calcium phosphate (BCP) are successfully used materials for biomedical applications due to their ability to promote bone integration. In this work calcium phosphate nanopowders were produced. Their morphology and crystalline phases were investigated in dependence of ultrasonic irradiation and addition of D-glucose and glycerol in the neutralization method. The results show that the neutralization method was effective to obtain ß-TCP and BCP with adjustable Ca:P ratios. The morphology and crystallinity of synthesized nanopowders are significantly affected by ultrasonic irradiation and additives. The grain size of the obtained nanopowders was decreased from 300nm to 50 nm by assistance of ultrasound.

Introduction

The interest in calcium phosphates for biomedical applications is increasing because theses ceramics exhibit high potential in the fields of orthopedic and dentistry, due to their chemical similarity to the mineral phase of bone tissue and their ability to promote bone integration. The most widely used calcium phosphates are hydroxyapatite, ($Ca_{10}(PO_4)_6(OH)_2$, HA) and beta tricalcium phosphate, ($Ca_3(PO_4)_2$, ß-TCP). They have been widely applied as biomaterial in the form of powder, granules, dense or porous bodies, and coatings for metallic and polymeric implants [1]. In the field of biomedical applications the rate of solubility is a very important factor. ß-TCP shows *in vivo* solubility 3-12 times higher than HA. Biphasic calcium phosphate (BCP), consisting of a mixture of HA and ß–TCP, has been considered as an ideal bone substitute due to its controllable degradability. It has been demonstrated that the bioactivity of these ceramics may be controlled by manipulating the HA/ß-TCP ratio [2]. The properties of the HA, ß-TCP and BCP powders such as crystal morphology, crystallinity, thermal stability, and solubility have been shown to be dependent on the route of fabrication. In a previous work synthesis by a neutralization method was reported to be suitable to obtain HA [3]. Ultrasonic irradiation was convincing as a promising tool to assist the synthetic reactions to prepare fine ceramic powders [4]. The aim of this work was to study the influence of ultrasonic irradiation and addition of D-glucose and glycerol on the synthesis, crystallinity and morphology of ß-TCP and BCP nanopowders.

Materials and Methods

Synthesis of calcium phosphate powders by neutralization was achieved by the addition of a 0.3 M aqueous solution of orthophosphoric acid (H_3PO_4) to 0.1 M aqueous suspension of calcium

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hydroxide ($Ca(OH)_2$) at room temperature. The reagents were mixed with a Ca/P molar ratio of 1.50 during magnetic stirring (N), or ultrasonic irradiation (-US). The aqueous suspension of $Ca(OH)_2$ was irradiated by ultrasound at two frequencies, 40 or 50 KHz. Additionally additives were used to prepare calcium phosphate, i.e. 40 wt% D-glucose (GLU) and 40 v% glycerol (GLY), respectively. The slurry was aged for 24h, filtrated, dried at 85 °C for 24h, and finally calcinated at 1000 °C for 3h. A white nanopowder was obtained. The main techniques used for powder characterization were Fourier transform infrared spectroscopy (FTIR), to determine the bands corresponding to functional groups, X-ray diffractometry (XRD) to obtain the crystalline phases and scanning electron microscopy (SEM) to evaluate the powder morphology.

Results and Dicussion

The synthesis of calcium phosphates by the neutralization methods with magnetic stirring (N) leads to the formation of an amorphous calcium phosphate (ACP) with a Ca/P molar ratio of 1.5. The results of the HT-XRD analysis reveal the presence of ACP in a temperature range between 100 and 600 °C, fig. 1. At room temperature ACP is only obtained under conditions of high supersaturation from solutions containing only calcium and phosphorous ions. ACP obtained in this manner was determined to have approximate formula $Ca_3(PO_4)_{1.87}(HPO_4)_{0.2}nH_2O$ [5]. At temperatures above 600 °C ACP transforms into ß-TCP, fig. 1, which is in good agreement with studies showing that pure ß-TCP cannot be directly obtained from aqueous systems but by calcination of ACP powders above 700 °C [5].

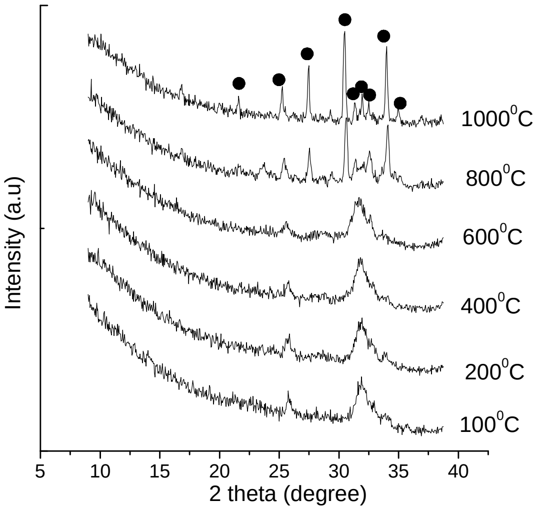

Fig. 1: HT-XRD patterns for the transformation of ACP produced by neutralization method into ß-TCP powders. (●) ß-TCP phase

The powders produced by neutralization method consisted of homogeneous spherical particles with an average grain size of 300 nm. Fig. 2 (A) and (C) show the morphologies of the powders dried at 85 °C for 24h and calcinated at 1000 °C for 3h, respectively. The specific surface area of the calcinated powders was detected to be 1.9 m^2/g. Ultrasound irradiation in neutralization method change the morphology, fig. 2(B). Calcination at 1000 °C for 3h leads to homogeneous spherical nanopowders with an average crystallite size of 50 nm and a specific surface area of 4.2 m^2/g, fig. 2 (D). The significant decrease in grain size can be assumed due to higher available energies during ultrasound irradiation, resulting in a disturbed growth of nuclei to their critical size.

Fig. 3 compares the calcinated powder XRD patterns obtained from the samples synthesized with and without assistance of ultrasound with a frequency of 50 KHz. From the N-patterns, no

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other crystalline phases than HA and ß-TCP were detected, while the powders produced by N-US presented mainly HA phase and secondary ß-TCP phase. Sonochemistry derives principally from acoustic cavitation, growth, and implosive collapse of bubbles in liquids. Cavitation serves as a means of concentrating the diffuse energy of sound [6]. The shock wave produces energy which could be able to generate ions and create free radicals. This can stimulate the reactivity of chemical species, resulting in the effective acceleration of heterogeneous reactions between liquid and solid reactants. Therefore the collapsing microbubbles may generate an energy which can rupture the molecular ionic bond and create reactive species as hydroxyl radicals [7]. Fig.4 shows FTIR spectra of CaP powders after calcination at 1000 °C for 3h. The OH absorption band at 633 cm^{-1} which is characteristic for HA phase is absent in N but present in the N-US.

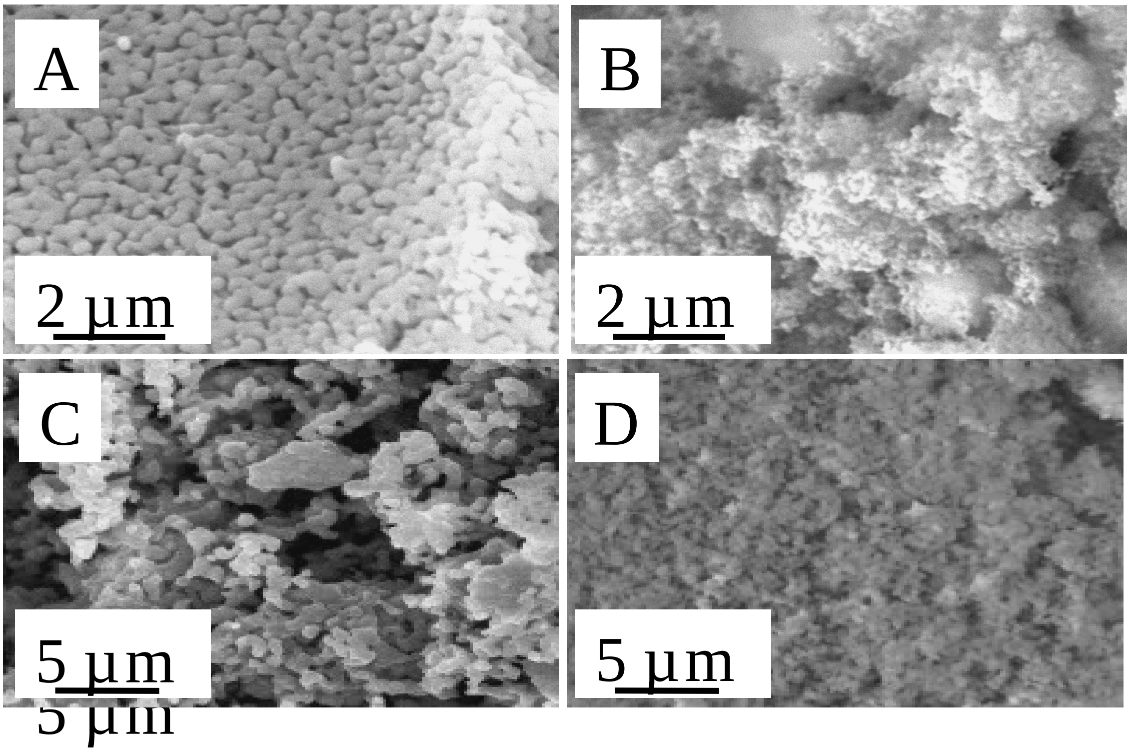

Fig.2: SEM micrographs of powders after drying at 85 °C for 24h (A) N and (B) N-US; and after calcination at 1000 °C for 3h (C) N and (D) N-US.

The influence of certain parameters such as frequency and viscosity by change of the concentration of additives was evaluated with a frequency of 40 KHz. In this experiment, the viscosity increased with the content of glucose (10-40 wt%) and glycerol (10-40 v%). It was observed that the viscosity impedes chemical activity of OH° by decreasing the formation of HA. The propagation of ultrasonic waves in water leads to H_2O sonolysis. One of the main consequences is the production of radical species, especially the very strong oxidizing hydroxyl radical OH^{o} [8]. However, it seems that the viscosity impedes chemical reactivity by decreasing the fluctuations in bubble diameter. The limit for formation of HA at 40 KHz were 40 wt% of GLU and 40 v% of GLY. New series of sonochemical experiments were repeated with this concentration of additives at a frequency of 50 KHz. Fig. 3 (GLU and GLU-US) shows powders with 40 wt% D-glucose additive which consist of ß-TCP phase, independent of magnetic stirring or ultrasound irradiation. Powders produced with 40 v% glycerol with magnetic stirring presented mainly ß-TCP phase with traces of HA, fig. 3 (GLY). HA phase was found as secondary phase in the ß-TCP produced by 40 v% glycerol, fig. 3 (GLY-US). GLY-US shows the OH absorption band at 633 cm^{-1}, characteristic

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of HA phase, fig. 4. The ultrasound frequency as well as the viscosity of the medium determine the type and intensity of cavitation.

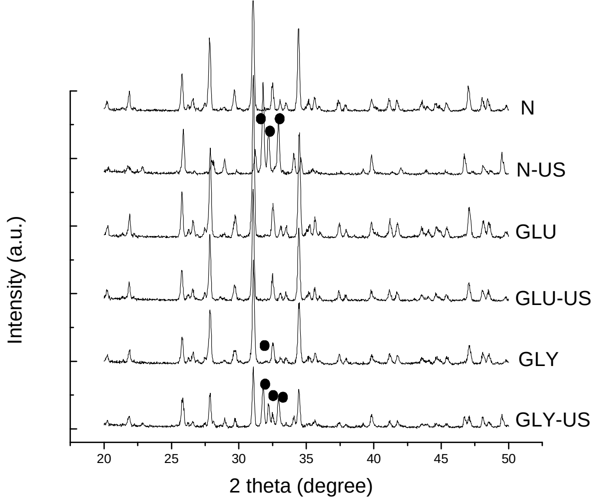

Fig. 3: XRD patterns of the powders, obtained and calcinated at 1000 ^{o}C for 3h. (•) HA phase.

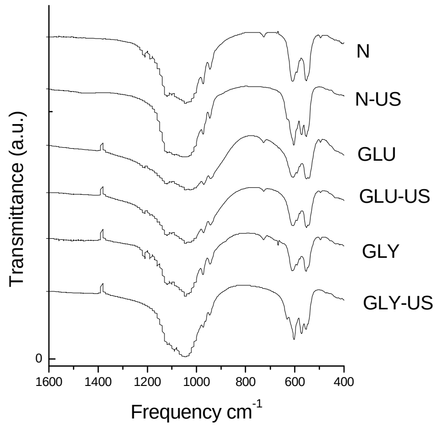

Fig.4: FTIR absorption spectra of powders obtained and calcinated at 1000 ^{o}C for 3h.

Conclusions

Precipitation of calcium phosphates by neutralization method was effective to obtain ß-TCP powder after calcination above 600 ^{o}C. The major contribution of this work is to emphasize that there is considerable potential in increasing the efficiency of sonochemical reactions in relation:

(i) with the production of nanopowders of calcium phosphate with a significant decreased grain size by neutralization method and ultrasound irradiation (50 KHz);

(ii) with the control of the formation of ß-TCP and HA by addition of D-glucose or glycerol to the solution, which leads to an increased viscosity, a minimized occurrence of microbubbles and thus prevents the formation of HA due to a reduced amount of OH° radicals;

(iii) with the production of BCP with adjustable ß-TCP/HA ratios which are important to control the bioactivity and the solubility of the composite.

Acknowledgements

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