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Ouzo effect—New simple nanoemulsion method for synthesis of strontium hydroxyapatite nanospheres

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ABSTRACT

Nanoemulsion technique was applied for synthesis of carbonated strontium hydroxyapatite (CSrHAp) at room temperature. X-ray powder diffraction analysis accompanied with Rietveld refinement reviled that synthesized powder were single-phase hydroxyapatite. Fourier transform infrared (FTIR) spectroscopy showed that the CSrHAp was A-type substitution. The carbonate amount substituting the hydroxide group in the synthesized apatite was estimated, from the corresponding CO_2 weight loss in the range 600–1100 °C. According to this empirical formula of as synthesized CHAp is $Sr_{10}(PO_4)_6(OH)_{0.60}(CO_3)_{0.70}$. These results were confirmed by the Rietveld refinement analysis. Using scanning electron microscopy analysis it was found that the synthesized CSrHAp particles were spherical in shape and that their sizes were in the nanometer range. Nanoemulsion strategy procedure provides a simple pathway to obtain single-phase CSrHAp.

1. Introduction

In recent years, carbonated strontium hydroxyapatite (CSrHAp), which is closely related to carbonated calcium hydroxyapatite, has attracted much attention as a biomaterial. CSrHAp has a good solubility [1], antiresorptive activity [2], osteoclast apoptosis [3], osteoblast stimulation [4], and ability to treat osteoporosis [5]. Recent success of treatments with strontium ranelate [6], which stimulates bone formation, decreases bone resorption and reduces the risk of vertebral fractures in postmenopausal osteoporosis, shows that strontium plays important role in stimulating the growth of osteoblasts and enhancing the formation of new bone. In addition, studies have shown that higher dose of strontium intake was significantly benefit to the formation of strontium-substituted apatite due to nucleation much easier than pure HAp, thus it may be the template to the formation of new bone [7] Therefore, strontium related compounds, as CSrHAp, may have the possibility to being used for bone regeneration.

CSrHAp are mostly used as powders and their behavior and usefulness depends on their crystal chemistry. On the other hand powder properties such as mean particle size, surface area and morphology can also have significant role in applications of these materials.

Among various methods that can be used for synthesis of CSrHAp, such as sol–gel [8], hydrothermal [9] and precipitation [10], nanoemulsion techniques can be ideal for the fabrication of nano-biomaterials, because it provides possibility to manipulate the structure of biomaterials at the molecular level and to carry out the reaction at low temperature.

It is well known that mixing of two immiscible liquids results generally in phase separation and formation of two pure liquid phases (for example: water + oil). In order to crate emulsion it is necessary to add some kind of surfactant (detergent in this example) and to perform some mechanical activation (stirring). But in some cases emulsification can occur spontaneously, even without surfactant. This effect is nanoemulsification and it is usually called the Ouzo effect [11,12]. Namely, the Ouzo is liquor which consists of anise oil dispersed in ethanol. When water is added to Ouzo, the dissolved anise oil spontaneously nucleates into many small droplets, without the help of surfactant. These small droplets scatter light causing the drink to appear milky white.

Nanoemulsions represent a special class of liquid disperse systems, defined as a dispersion consisting of oil, surfactant and an aqueous phase. These solid liquid solutions are optically isotropic

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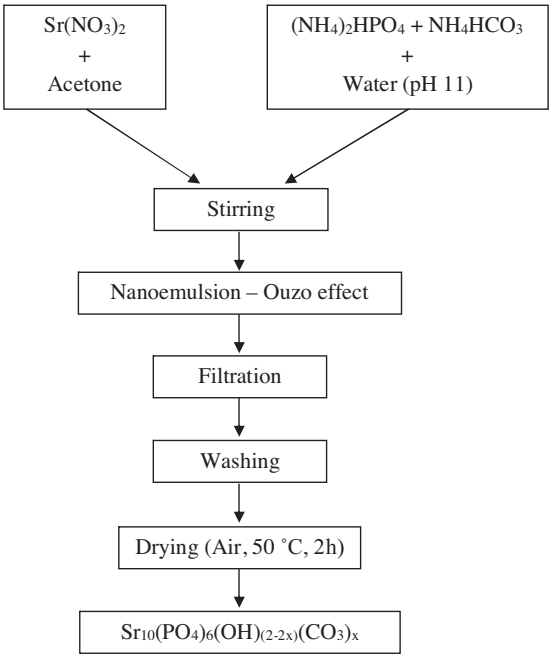

Fig. 1. Flow diagram for preparation nano-sized CSrHAp spheres using the nanoemulsion technique.

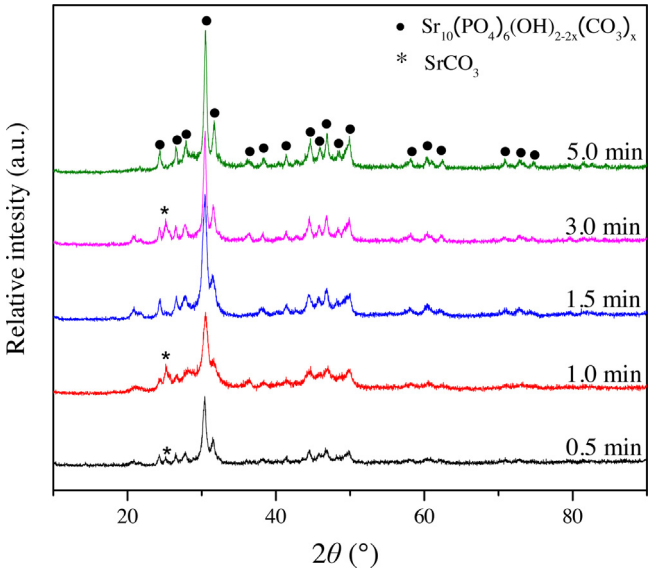

Fig. 2. XRPD patterns of synthesized CSrHAp samples, for different stirring times during synthesis.

and thermo-dynamically stable, usually with droplet diameter less than 100 nm [13], or according to some definitions within the range of 20–200 nm [14]. Among various methods that can be used for synthesis of CSrHAp nanoemulsion techniques can be ideal for the fabrication of nano-biomaterials, because this method can produce spherical nanoparticles with small size of droplets [15]. Nanoemulsions offer the possibility of obtaining microemulsion-like dispersions without the need to use high surfactant concentrations or even without the use of any surfactant at all. Emulsification occurs almost simultaneously in the entire volume, thus requiring much less energy consumption in large-scale production. Due to the small size of droplets of the internal phase, nanoemulsions have already found diverse applications in the transdermal transport of drugs and biologically active substances. This is of special interest for specialists in pharmaceutical and cosmetic industries. In addition to medicine, the most promising fields of application of nanoemulsions include agrochemical, paint and varnish and petroleum industries [16].

The aim of this work was to demonstrate a simple strategy for the synthesis of nanospheres of strontium hydroxyapatite in which hydroxyl group is partially substituted with carbonate group [$Sr_{10}(PO_4)_6(OH)_{(2-2x)}(CO_3)_x$] via a nanemulsion route. According to the author's knowledge this method was used for the very first time for synthesis of this kind of hydroxyapatite. A simple, low temperature oil-in-water method for the synthesis of pure nano-SrHAp was developed. The composition and morphology of the synthesized nano-SrHAp were investigated using X-ray diffraction (XRD), Ritveld structural and microstructural refinement, Fourier-transform infrared (FTIR) spectroscopy, differential thermal analysis (DTA/TG) and scanning electron microscopy (SEM).

2. Experimental methods

SrCHAp nanoparticles were synthesized using analytical grade $Sr(NO_3)_2$ (Riedel-de Haën, 99% purity), $(NH_4)_2HPO_4$ (Riedel-de Haën, 99% purity) and NH_4HCO_3 (Sigma–Aldrich, 99% purity). The solvent used for making nanoemulsions was analytical grade acetone. The synthesis process is illustrated in Fig. 1. An acetone solution of $Sr(NO_3)_2$ was mixed with an aqueous solution of $(NH_4)_2HPO_4$ and NH_4HCO_3 at a molar ratio of $Ca^{2+}:PO_4^{3-}:CO_3^{2-} = 1.67:1:0.5$ using a magnetic stirrer. The aqueous solution was adjusted to pH 11 with sodium hydroxide (1 M) prior to mixing. No surfactant was used in all synthesis processes. Different stirring time (0.5, 1, 1.5, 3 and 5 min) was performed in order to investigate it influence on crystallization of SrCHAp. The resultant nanoprecipitates in the solutions were immediately filtered using a vacuum filtration set to avoid particle agglomeration and then washed three times using ultra-pure deionized water. Finally, the slurry of nanoprecipitates was dried out in the oven at 50 °C in order to obtain dry powder.

The phase purity and crystallinity of apatite powders produced were examined using X-ray diffraction (Raguku Ultima IV, Japan). The X-ray beam was nickel-filtered CuKα_1 radiation ($\lambda = 0.1540$ nm, operating at 40 kV and 40 mA). XRD data were collected from 20 to 120° (2θ) at a scanning rate of 2°/min. A refinement of the structure of strontium hydroxide phosphate was undertaken in order to elucidate the crystal structure and microstructure of hydroxyapatite. The refinement was performed with the FullProf computer program [17–19] which adopts the Rietveld calculation method. The TCH pseudo-Voigt profile function was used. To take instrumental broadening into account, the XRD pattern of a standard specimen CeO_2 was fitted by the convolution of the experimental TCH pseudo-Voigt function [20].

Fourier transform infrared spectroscopy (FTIR) was performed to determine the presence of functional groups such as OH^- groups and CO_3^{2-} groups in partially substituted apatite. FTIR spectra were recorded in the absorbance mode using a BOMEM Michelson Series MB FTIR spectrometer set to give undeformed spectra. The resolution was 4 cm^{-1} in the 400–4000 cm^{-1} analyzed range. The spectra were obtained at room temperature from KBr pressed pellets prepared by mixing 1.5 mg of a sample with 150 mg of KBr.

The morphology of dried nanoprecipitates was characterized by a Tescan MIRA3 field emission gun scanning electron microscope (SEM), with electron energies of 20 kV in high vacuum. The samples used for SEM characterization were coated with 5 nm thin layer of Au/Pd using a standard sputtering technique. The results from SEM measurements show the sample area of 2.5 μm × 2.5 μm (275 k× magnification). Semi-quantitative anal-