



Alternating current electric field modified synthesis of hydroxyapatite bioceramics

Ž. Janičijević^{a,b,*}, M.J. Lukić^b, L. Veselinović^b

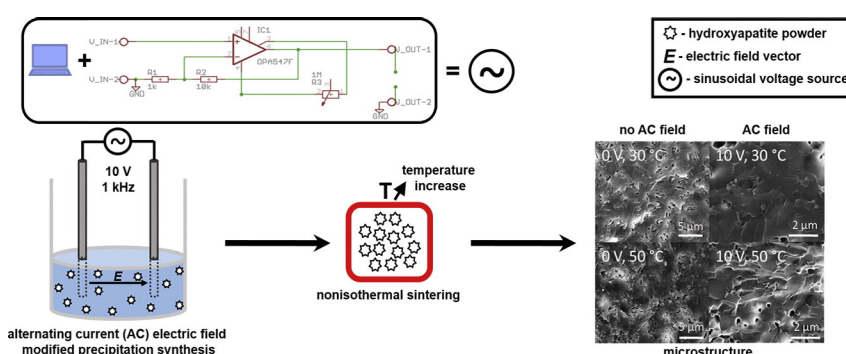
^a School of Electrical Engineering, University of Belgrade, Bulevar kralja Aleksandra 73, 11120 Belgrade, Serbia

^b Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Knez Mihailova 35/IV, 11000 Belgrade, Serbia

HIGHLIGHTS

- Low-cost and reliable electrical setup was designed to modify material synthesis.
- Alternating current voltage excitation can modulate hydroxyapatite precipitation.
- Crystallization of hydroxyapatite was improved by voltage excitation.
- Synthesized hydroxyapatite exhibited enhanced sintering and thermal stability.

GRAPHICAL ABSTRACT



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ABSTRACT

This study presents an innovative approach towards wet chemical synthesis of hydroxyapatite bioceramics by application of alternating current (AC) electric field during the synthesis at low and intermediate temperatures. Specially designed low-cost electrical setup provided stable, reliable and modular system which supplied electric energy within the reaction volume as characterized by computer simulation of reaction conditions. Energy introduced through external excitation (alternating voltage amplitude of 10 V and frequency of 1 kHz) influenced crystallization, ionic composition, sintering behavior of hydroxyapatite powders, microstructure and final phase composition of sintered ceramics. Crystallite size in [002] crystallographic direction increased with electric field assistance regardless of the synthesis temperature. Non-isothermal sintering studies showed significantly improved densification and implied better thermal stability of powders synthesized in the presence of AC field, shifting the Ca/P ratio towards stoichiometric one. Vibrational spectroscopy analysis indicated the role of charge, mobility and effective ionic radius of present ions in transferring the energy supplied with external field influencing further thermal stability of the crystal lattice. Microstructural investigation and phase composition analysis suggested that application of AC electric field during the synthesis of nanocrystalline hydroxyapatite improved material properties and offered potential for tailoring macro/micro-porosity with precise modulation of electrical parameters.

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1. Introduction

Hydroxyapatite (HAp) is an important ceramic biomaterial found in nature as a mineral phase of biological bones and teeth [1]. It is a

* Corresponding author at: School of Electrical Engineering, University of Belgrade, Bulevar kralja Aleksandra 73, 11120 Belgrade, Serbia.
E-mail address: zeljkoj@etf.rs (Ž. Janičijević).

relatively large polar crystal composed of several inorganic ionic constituents. One of the common routes for the synthesis of HAp nanoparticles is the wet chemical precipitation method. Being the most abundant HAp preparation route, chemical precipitation synthesis could provide diverse morphology of particles, but often low-crystalline material, with variable phase purity and stoichiometry [2]. Synthesis protocol of the basic method was optimized in the past in terms of reagents and processing parameters [3,4]. This method is popular due to its low-cost, simplicity, high yield and potentially good sinterability, however, main disadvantages preventing its wider use are difficult control of particle size and extensive agglomeration [5].

Many researchers have attempted to include physical methods in the process of HAp synthesis, such as: vibro-milling [6], laser ablation [7,8], and radio frequency induction plasma [9] in order to improve material properties. Modification of material synthesis using physical fields could offer a higher degree of control over the synthesis process and properties of particles and sintered ceramics compared to the traditional chemical approaches [10,11]. Physical field parameters can be accurately adjusted and modulated in real-time. Since the change in the field parameters can be implemented digitally, reproducibility of the modification effects can be easily ensured. Wet chemical synthesis of HAp was successfully modified in the past using ultrasound (the alternating field of mechanical waves) [12–14] and microwaves (high frequency electromagnetic radiation) [15,16]. Recently, the effect of applied direct current (DC) and alternating current (AC) electric fields on material synthesis and properties has drawn significant attention [17–20]. AC electric field application can offer several modification parameters, such as: amplitude, frequency and waveform shape. Modification with the AC electric field may contribute to the spatial localization and directionality of ionic interactions during crystallization. Use of AC electric fields does not enhance and direct overall mass transport, but rather relies on different modulation mechanisms compared to the DC electric field. Application of AC electric field to the electrolyte solution leads to the electric field-induced dipolar interactions and produces local electro-hydrodynamic flows while minimizing electrochemical and electroosmotic effects [21]. HAp is a good candidate for AC electric field modification in aqueous systems. Gradient of electric permittivity at HAp/water interface and heterogeneous ionic composition of HAp provide the possibility for the electric field to affect particle orientation. Various responsiveness degrees of ionic reactants to the applied electric field indicate the potential for anisotropic crystal growth and alterations in HAp ionic composition and stoichiometry. To the best of our knowledge, studies of AC electric field effects on the synthesis of pure HAp have not been previously reported in the literature.

Through the combined scientific and engineering approach we have designed and implemented an inexpensive modular electronic device for the modification of HAp synthesis with AC electric fields. In our approach, the wet chemical precipitation method is modified by the internal application of the AC electric field which is digitally controlled by the dedicated experimental setup. We demonstrate that the presence of AC electric field during the synthesis process can alter the relative ratio of ionic species at specific positions in HAp crystal lattice, affect crystallite size and improve the sintering behavior of pure HAp.

2. Materials and methods

2.1. Electrical setup for voltage excitation

Voltage excitation of the reaction system was executed using the in-house built custom electrical setup presented in Fig. 1 (a). Design of the setup is based on the OPA547 operational amplifier and a sound card digital-to-analog converter (SC DAC). Waveform shape, amplitude and frequency at the SC DAC output were adjusted manually in LabVIEW based software (Soundcard Scope, version 1.41). The excitation voltage signal was amplified using the non-inverting operational amplifier configuration with the gain of 11 and the output current was limited by the

trimmer potentiometer. The constructed excitation device can provide accurate and stable sinusoidal AC voltage excitation within the amplitude range of (0.1–10) V and frequency range of (0.01–10) kHz having a continuous current output amplitude of up to 0.5 A. Low cost, modularity, reliability and simplicity of the setup make it very attractive and suitable for versatile research applications in materials science. Design details and specific considerations are discussed in the supplementary section “**Electronic device design**”.

2.2. Preparation of materials and physico-chemical characterization

Nanocrystalline HAp powders were synthesized using the wet precipitation method assisted with AC electric field. The synthesis was performed in an open reactor under atmospheric pressure at two different temperatures, 30 and 50 °C, and modified with the AC sinusoidal voltage excitation applied internally between the two electrodes immersed in the reaction mixture (Fig. 1 (b)). The source of calcium ions was $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Fluka, Germany) while the source of phosphate ions was $\text{NH}_4\text{H}_2\text{PO}_4$ (VWR International, Belgium). The pH of the reaction mixture was adjusted with 25% NH_4OH solution (NRK inženjering, Serbia). In a typical procedure, 1 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.292 g of $\text{NH}_4\text{H}_2\text{PO}_4$ (initial Ca/P ratio of 1.67) were dissolved in 100 ml and 22.5 ml of distilled water, respectively, and both solutions were brought to the required temperature. The phosphate solution was subsequently mixed with 2.5 ml of NH_4OH . Two cylindrical stainless steel electrodes of 3.2 mm diameter were immersed into the solution of calcium ions, placed in a 250 ml beaker up to the initial depth of 16 mm, and positioned at a fixed distance of 40 mm by the electrode holder built in-house. Sinusoidal AC voltage excitation with the amplitude of 10 V and frequency of 1 kHz was applied between the electrodes to the solution of calcium ions having initial pH of 5.8 from a digitally controlled custom built voltage source. Choice of electrical excitation parameters was based on the results of preliminary experimental tests (see supplementary section “**Optimization of electrical excitation parameters**”). In order to induce precipitation, solution of phosphate ions was slowly added to the solution of calcium ions at a rate of 1.6 ml/min. After the addition of phosphate ions, the slurry had a pH of 9.8. The reaction mixture was continuously stirred at a speed of 200 rpm and kept at constant temperature under the stable AC voltage excitation for the entire reaction time of 3 h. Obtained white precipitate was separated from the supernatant by decantation, and then washed with distilled water to remove residual nitrate and ammonium ions until the decanting supernatant reached neutral pH. The precipitate was not aged in the basic mother solution since the initial effect of the applied electric field could be masked. Afterwards, the slurry was filtered and dried for 18 h under atmospheric pressure at 60 °C in the oven. The dry precipitate was ultimately ground in a mortar using a pestle. The final product was white powder. Samples of HAp powder were prepared under the same experimental conditions in the absence of AC voltage excitation as control series.

Non-isothermal sintering studies were performed by dilatometric analysis (TMA, Setaram Evolution, France), with heating and cooling rates of 20 °C/min up to the temperature of 1200 °C. The load applied between the contact probe and green pellet was 5 g in each experiment. The change of height of the specimen, h , was recorded and compared to the initial height, h_0 . XRD analysis of synthesized powders and sintered pellets was carried out using X-ray diffraction (Philips PW-1050) in 2θ range from 15 to 60°, with the step of 0.05° and dwell time of 3 s. Crystallite size in [002] crystallographic direction was calculated using Scherrer's equation. Calculation of the unit cell parameters was accomplished with the LSUCRI program adapted for the personal computer [22]. The amount of calcium phosphate phases after sintering was calculated according to the intensities of the strongest reflections of HAp and β -TCP which was further used for semi-quantitative determination of Ca/P ratio in the materials [23]. Final densities of sintered materials were calculated using the geometrical and weight measurements on

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