

HYDROTHERMAL SYNTHESIS OF HYDROXYAPATITE WITH TARTARIC ACID

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Abstract

The hydrothermal synthesis of hydroxyapatite (HA) with addition of tartaric acid (TA) is presented in the paper. The role of tartaric acid is to form a complex with the Ca ions and to help in tailoring the crystallization behavior of hydroxyapatite. A comparison is made between two situations: one is characterized by the addition of tartaric acid after the precipitation of hydroxyapatite, and the other is defined by tartaric acid being added to the Ca precursor, followed by the addition of the P precursor. The crystalline particles resulted were studied by means of XRD, FTIR, SEM and TEM, and it was concluded that they consist in hexagonal lamellar crystals with lengths < 200 nm and widths < 50 nm. The difference between the two cases is that the crystallinity degree, the uniformity in crystal dimensions and the aspect ratio are higher when TA was added before the precipitation rather than to the precipitated HA. The dimensions of the achieved crystals are similar to the mineral grains found in the hard tissues of the human body.

Introduction

Synthetic hydroxyapatite represents a widely used biocompatible and bioactive material for human implants [1], due to its similarity with the natural hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), which is present in a high amount in the hard tissues of the human body. HA has been synthesized by a variety of methods like precipitation, hydrolysis, sol-gel, solid state reactions, etc [2]; among these methods, in recent years, the hydrothermal method has gained an increasingly important role due to a series of advantages, one of them being the fact that the properties of the final product, such as: crystallinity degree, morphology and size of particles [3], can be tailored.

A different approach in modeling the properties of HA ceramic powders is the addition of some conditioners, such as organic acids. It has been reported that the addition of organic acids, like citric acid, ascorbic acid, tartaric acid, etc, will have an inhibitory effect on the crystallization of HA [4,5], probably due to the attachment of the organic ions to the active growing sites of the newly-formed nuclei. The presumed chemical mechanism (described by us in [6]) implies the complexation of the metallic ions by the organic ions and lowering the number of active Ca sites onto the crystal seeds; as a result of this inhibition, particles with higher aspect ratio are expected to form.

The purpose of the present work was the use of a small concentration of tartaric acid in order to study its influence on the hydrothermal synthesis of hydroxyapatite, when it is added in different stages of the synthesis process, in a neutral environment. In our knowledge, no studies of hydrothermal synthesis of HA with organic acids have been presented in the literature.

Experimental

The chemicals used for the synthesis are $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich) as Ca precursor, $(\text{NH}_4)_2\text{HPO}_4$ (Merck) as P precursor and racemic tartaric acid (TA) $\text{C}_4\text{H}_6\text{O}_6$ (Merck), all brought to 0.05M solutions. Aliquots were used so as to maintain the molar ratio of 1.66 between the Ca and P (because this is the stoichiometric ratio of hydroxyapatite), while the tartaric acid molar ratio is 1.25 in relationship to phosphorus.

In order to establish what is the best stage to add the tartaric acid, this was added either after the HA precipitation, or between the mixing of the two precursors. For the first sample (named HA_T_1), the P precursor was added to the Ca precursor and then the tartaric acid was mixed with the solution, while for the second sample (named HA_T_2), the tartaric acid was mixed with Ca, then the P precursor was added. The pH value was maintained around 7 by ammonia addition.

After the admixture of the reactants and HA precipitation, the solution + precipitate were closed in Teflon liners are heated at 220°C for 24 h. After cooling to room temperature, the samples were extracted and washed about 6 times with double distilled water, then dried in the oven at 60°C for 4 h.

The physico-chemical characterization of the synthesized samples was achieved using the equipments:

- XRD – PANalytical X'Pert Pro MPD Diffractometer equipped with a Cu anode and PixCEL detector, powder samples supported on zero background silicone holders, working parameters: 45 kV, 30 mA
- FT-IR: Vertex 70 Spectrometer from Bruker, within the range $4000\text{--}400\text{ cm}^{-1}$ with a 4 cm^{-1} resolution, using transmission technique. For sample preparation, the KBr pressed disc technique was used, mixing approx. 1 mg of each sample with 200 mg KBr. The discs were introduced in the spectrometer immediately, in order to minimize the amount of absorbed water
- SEM: Inspect S (FEI Company); powder samples were supported on carbon tape
- TEM: Titan G2 80–200 (FEI Company), accelerating voltage: 200 kV. Samples were prepared by depositing a droplet of suspension (ethylic alcohol) on 200 mesh copper grids covered with lacey carbon film.

Results and discussion

The XRD patterns for the two samples are presented in Figure 1:

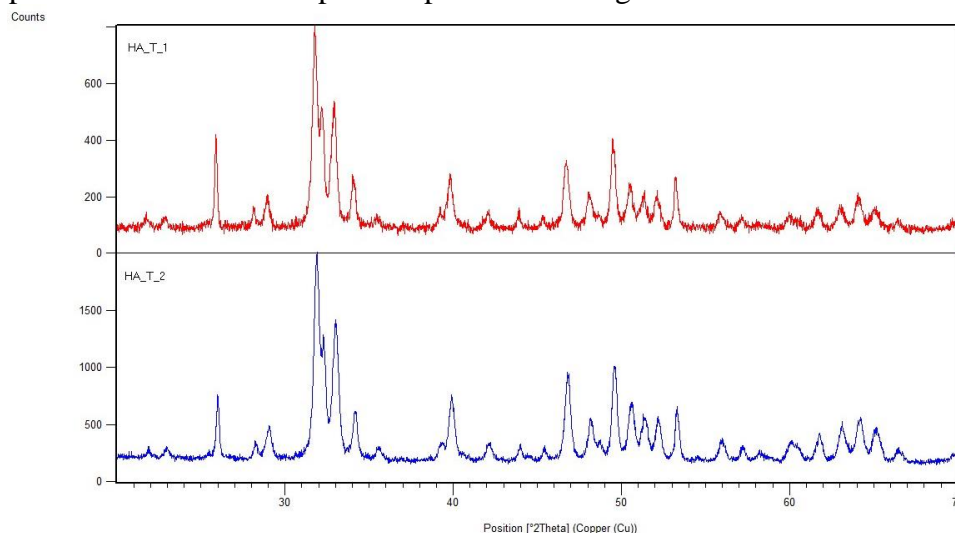


Fig 1 The XRD patterns of the samples HA_T_1 and HA_T_2

The patterns present the regular lines of crystalline hydroxyapatite, confirming the identity of the synthesized samples. No other crystalline phase is present in the synthesis products. By comparing the intensity of the peaks, it can be noticed that when TA was added after the HA precipitation, the final product is less crystalline than the sample achieved by adding TA to the Ca precursor. Preferential orientation in respect to the *c* crystallographic direction can be observed for the sample HA_T_1.

The FT-IR patterns are presented in Figure 2 and confirm the formation of hydroxyapatite, without other calcium phosphates being present. The characteristic vibrational domains are [7]: ν_1 (around 950 cm^{-1}), ν_2 ($400\text{--}470\text{ cm}^{-1}$), ν_3 ($1000\text{--}1150\text{ cm}^{-1}$) and ν_4 ($500\text{--}620\text{ cm}^{-1}$). The broad absorption band at around 3400 cm^{-1} and the band at 1630 cm^{-1} are characteristic for the adsorbed water molecules, and the sharp band at 3570 cm^{-1} represent the free OH anions present in the crystalline lattice. The sharp band in the region $1379\text{--}1384\text{ cm}^{-1}$ does not belong to HA and is assigned to the deformation vibration of the C-O bond [8], suggesting the adhesion of the tartrate ion to the HA crystals. This adhesion phenomenon is present in both studied cases and is in agreement with the results of other research groups, as mentioned before.

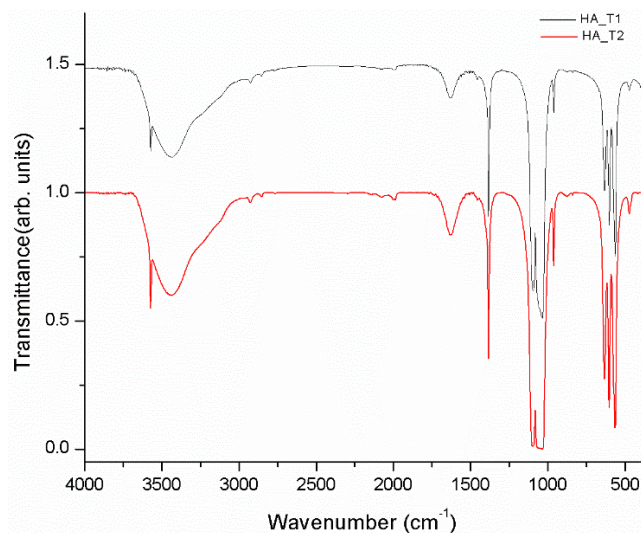


Fig 2 FT-IR patterns of the two HA samples

The morphology of the prepared HA samples was studied by SEM, the images being presented in Figure 3. The both samples present a high degree of compactness; not much information is available due to this agglomeration, so samples were analyzed by TEM (Figure 4). It can be observed in the TEM images that the crystalline particles are lamellar in shape, but the lamellas are not rectangle-shaped. Instead, a deformed hexagonal shape can be observed, with unequal sides. Regarding the size of the crystals, the two samples have similar dimensions, namely lengths of less than 200 nm and widths of less than 50 nm. The sample HA_T_2 seem to be more uniform regarding the shape and dimensions of the crystals, compared to the sample HA_T_1, and the aspect ratio appears to be better for the sample prepared with TA added to the Ca precursor.

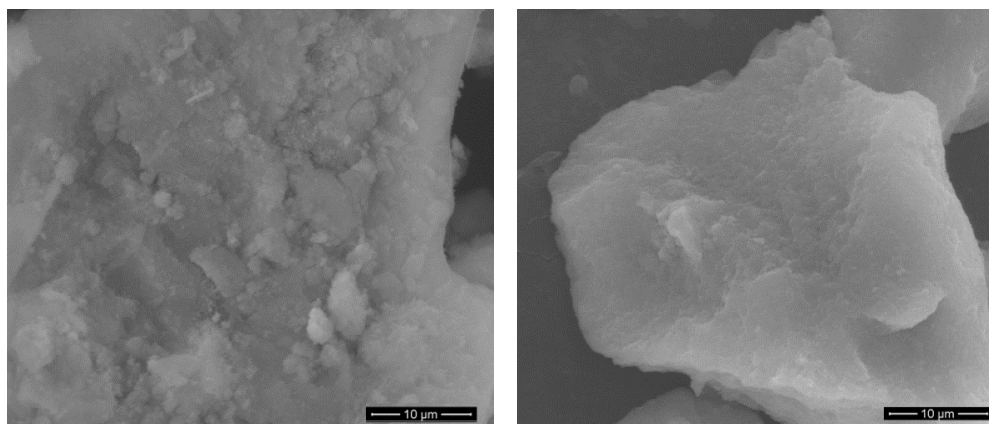


Fig 3 SEM images of the samples: left – HA_T_1; right – HA_T_2

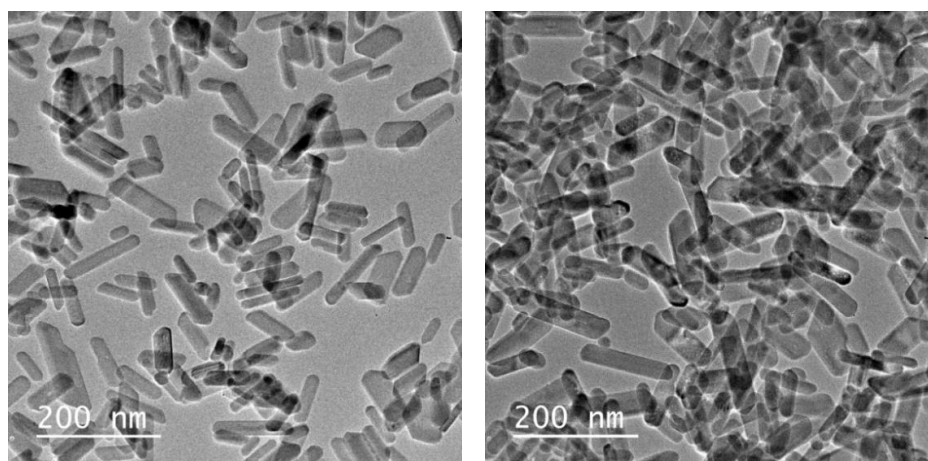


Fig 4 TEM images of the samples: left – HA_T_1; right – HA_T_2

Conclusion

Hexagonal lamellas of crystalline hydroxyapatite were synthesized by aqueous precipitation in neutral environment and crystallization by hydrothermal method at 220°C for 24h. Tartaric acid was added either after the HA precipitation or between the mixing of the Ca and P precursors. The formation of a complex between the tartrate ions and the Ca ions has resulted in a more crystalline hydroxyapatite, with more uniform particles shape and dimensions, compared with the crystalline particles achieved when tartaric acid was added after the precipitation of the HA. The dimensions of the achieved crystals are similar to the mineral grains found in the hard tissues of the human body.

References

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