Electrochemical synthesis of nanosized hydroxyapatite

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Bone is the major calcified tissue of the human body. Microscopically, the constituent building blocks of bone are mineralized collagen fibrils of around 80 nm thickness and up to tens of microns in length. These fibrils are true nanocomposites of biological apatite and molecules of type I collagen. The crystals of biological apatite in bone are always platelet-like (elongated along the crystallographic *c* axis) and very thin; about 2 nm [1, 2]. Calcium phosphate-based materials, especially bioactive hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$), are used as bone substitute material due to their chemical and structural resemblance to the mineral portion of bone. The preparation of hydroxyapatite powders with controlled characteristics of morphology, stoichiometry, crystallinity and, particularly, size in the nanometer range, is key for the production of a variety of biomaterials, i.e., bioceramics, composites, etc. [2–4].

Various synthesis methods have been used for HAp microsized powders, ranging from solid-state reactions, precipitation by homogeneous solutions, hydrolysis of calcium phosphate salts, emulsions to sol–gel [5–15]. In particular, it is known that the use of homogeneous Ca/EDTA/PO_4^{3-} solutions for hydrothermal synthesis produces HAp particles in the micrometer-size range [16–23]. In this article, we report how the electrolysis of a Ca/EDTA/PO_4^{3-} homogeneous solution produces controlled nanosized hydroxyapatite solids. The electrolysis process was performed by using Ca/EDTA/PO_4^{3-} at a concentration relationship of 0.25/0.25/0.15 M, with platinum rectangular electrodes, a current density of 137 mA/cm^2, and a constant stirring at 25 °C during 3 hr. The solid precipitates are produced from solutions at initial pH values of 5.0, 7.0, and 9.0, over the cathode. As the electrolysis process occurs, pH is increased by 2.8 and 2.1 units for the solutions with an initial of pH 5.0 and pH 7.0, respectively. For cases of the solution of pH 9.0, the pH changed by only 0.1 units during the process. The specimens were characterized with Transmission Electron Microscopy (TEM), Electron Dispersion Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD).

According to the XRD results, all three solutions yield HAp as the only phase. Fig. 1 corresponds to a pH 7.0 sample, typical of all XRD obtained for the three cases. EDS analysis showed that the Ca/P ratios were 1.46, 1.55, and 1.60, at pH 5.0, 7.0, and 9.0, respectively, indicating that all precipitates are calcium-deficient. This fact could be due to the presence of CO_3^{2-} and HPO_4^{2-}, as shown by the infrared spectra. The produced solid precipitates show platelet-like crystallites with lengths varying between 40 and 250 nm. The solid precipitate obtained at pH 5.0 shows crystallites with sizes varying between 150 and 250 nm, meanwhile in the obtained precipitate at pH 7.0, crystallite sizes vary between 50 and 80 nm. Fig. 2 corresponds to the solid precipitate obtained at pH 9.0 showing crystallites having sizes varying between 30 and 50 nm. Electrolysis using a much lower current density of 55 mA/cm^2 at pH 7.0 produces a no-

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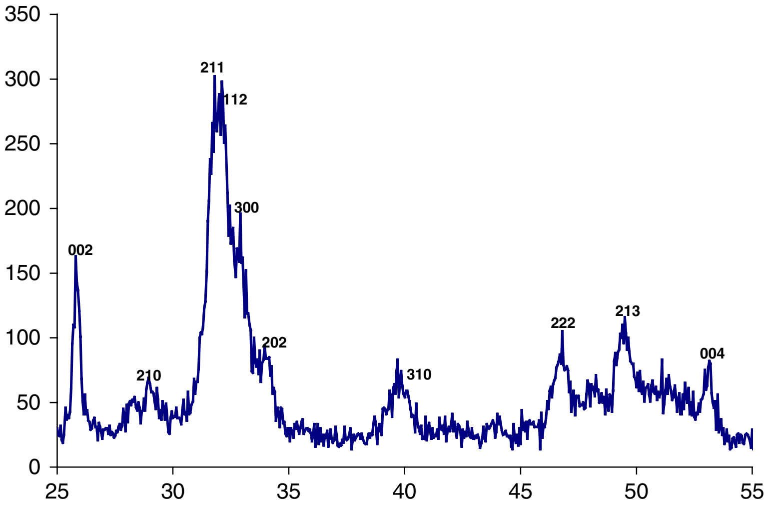

Figure 1 XRD of sample prepared at pH 7. It is typical of all samples prepared at different pH values and current density of 137 mA/cm^2. Crystallographic planes are identified. The figure shows that the solids obtained are indeed HAp and with a high degree of crystallinity.

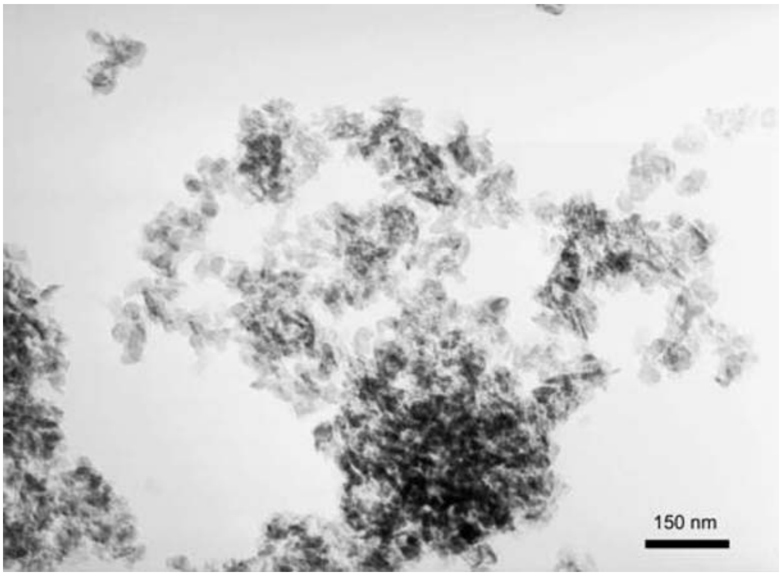

Figure 2 The solid precipitate obtained at pH 9 is formed by platelet-like crystallites ranging in size from 30 to 50 nm.

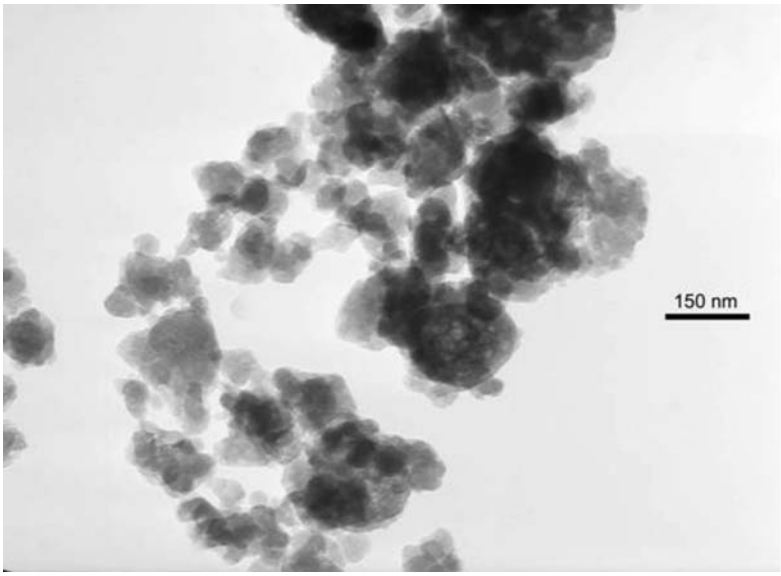

Figure 3 The solid precipitate by electrolysis using a much lower current density of 55 mA/cm^2 at pH 7.0 produces rounded corpuscles instead of platelet shaped crystallites.

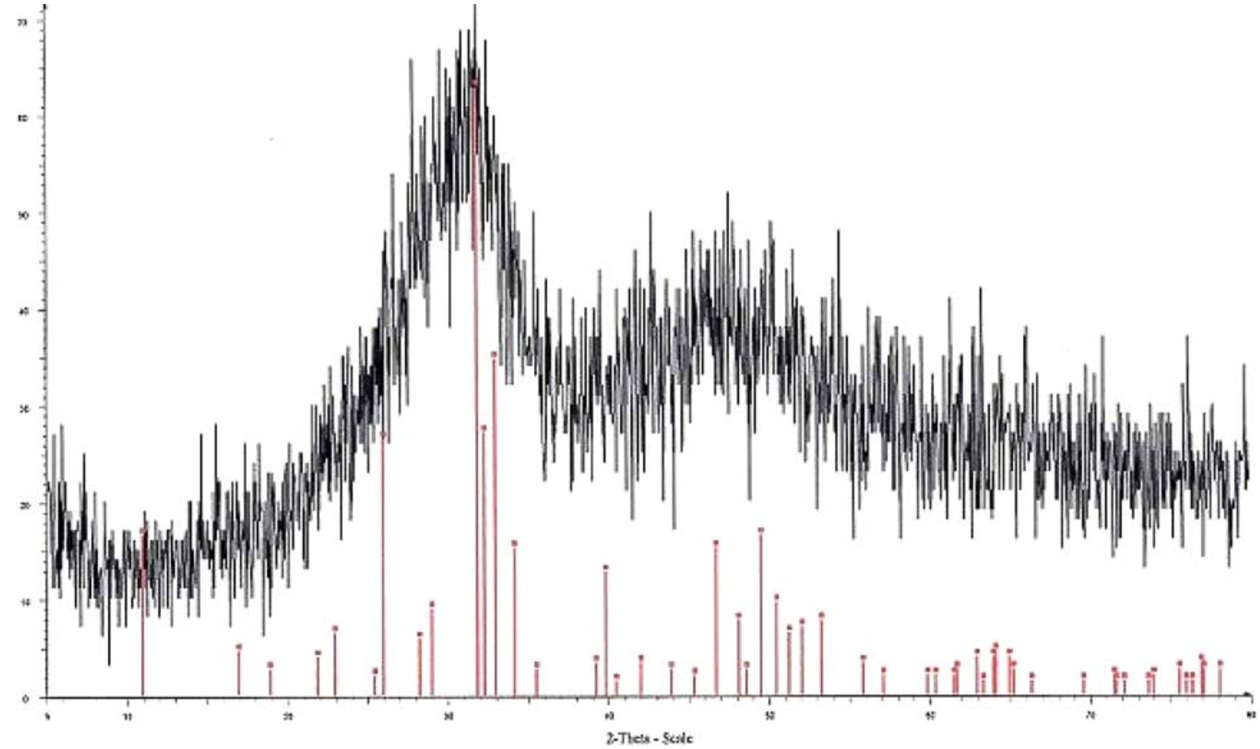

Figure 4 XRD for precipitate obtained at pH 7 and current density of 55 mA/cm^2 exhibits only very broad and few peaks that correspond to HAp . This suggests a lower degree of crystallinity. However, no peaks that would correspond to other substance appear.

table change in morphology, rounded corpuscles (Fig. 3) and XRD exhibiting very broad and few peaks that correspond to HAp (Fig. 4). This suggests a lower degree of crystallinity.

In conclusion, we report how a simple electrolysis reaction of Ca/EDTA/PO_4^{3-} homogeneous solutions, produces nanosized platelet-like hydroxyapatite (similar to actual biological apatite) as solid precipitates. Crystallite sizes strongly depend on the initial pH value, which decrease with increasing pH, all being in the nanosize range. Preliminary studies changing the current density demonstrate the possibility of controlling crystallinity and morphology of the HAp obtained. Finally, we must stress the fact that the use of EDTA as a ligand for calcium allows experiments to be carried out at high calcium and phophate ion concentrations (Ca/EDTA/PO_4^{3-} at a concentration relationship of 0.25/0.25/0.15 M), and a wide range of pH values. It has been reported that under hydrothermal conditions, homogeneous Ca/EDTA/PO_4^{3-} solutions at the aforementioned relationship produce HAp whiskers [23, 24], however the same solution under electrolysis produces nanometric HAp. The formation mechanism for this reaction requires the liberation of Ca^{2+} from EDTA and the generation of OH^- ions through water reduction and ionic migration towards the electrodes. The entire process occurs on the cathode surface. Studies at other pH values, different current densities, electrodes with different shape and material, and solution concentrations, in order to try to better understand the reaction will be reported separately.

Acknowledgments

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