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Chemically-induced nucleation of hydroxyapatite at low temperature

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Calcium phosphates, particularly of the apatite type, have attracted growing interest because of their application as biomaterials [1–3] and a number of different methodologies for producing synthetic calcium phosphates are available in the literature, ranging from updates of long-known techniques, to reports on novel synthetic routes [4–11]. Special effort has been dedicated to hydroxyapatite (HAp), due to its being the main inorganic component of living calcified tissue [1, 2]. In fact, most synthesis approaches for producing good quality HAp are based on its precipitation in aqueous solutions, where the specific phosphates phases, stoichiometry, degree of crystallinity, morphology and other relevant characteristics are known to strongly depend on physico-chemical parameters such as pH, concentration of reactants, temperature, etc. [4–17], which are difficult to control in practice. Recently, the synthesis of HAp from the decomposition of chelating agents, such as lactic acid or EDTA [11–16] has proven an excellent alternative for controlling the Ca/P relationship, a key parameter if materials of biomedical relevance are to be prepared. In this present article, we report how the nucleation of HAp can be conveniently induced, at low temperatures and in acidic conditions, by the addition of nanosized silica particles.

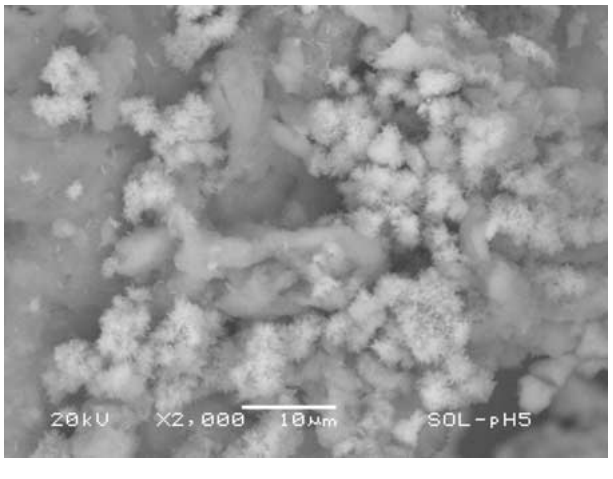

Figure 1 SEM micrograph of the sample prepared at pH = 5.

A Ca/EDTA/PO_4^{3-} homogeneous solution with a concentration relationship of 0.25/0.25/0.15 was prepared as previously reported [18, 19]. Then, silica nanoparticles were *in situ* prepared in the same above solution, at 100 °C, from the hydrolysis of TEOS, similar to the standard sol-gel technique. The effect of various pH values (namely 5, 7 and 9) was significant for the final characteristics of the product, as can be observed in the SEM micrograph of Fig. 1 (pH = 5), where HAp agglomerates, with average size below 10 μm, are evenly

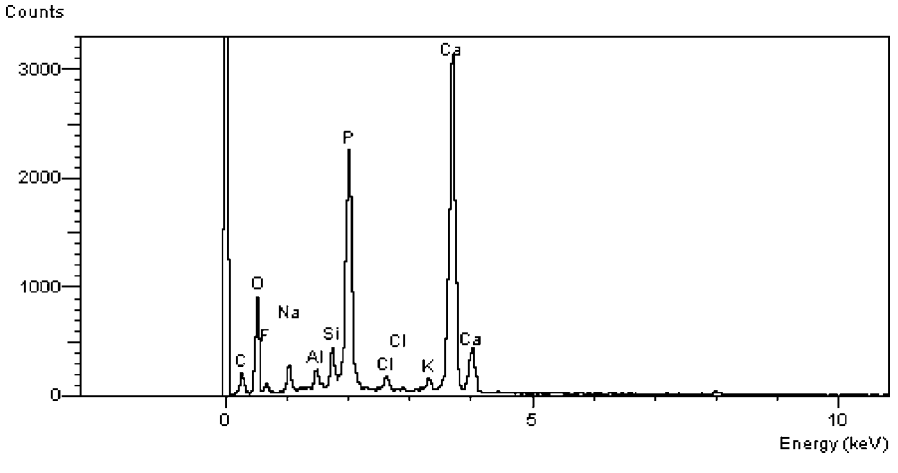

Figure 2 EDS spectrum of the sample of Fig. 1.

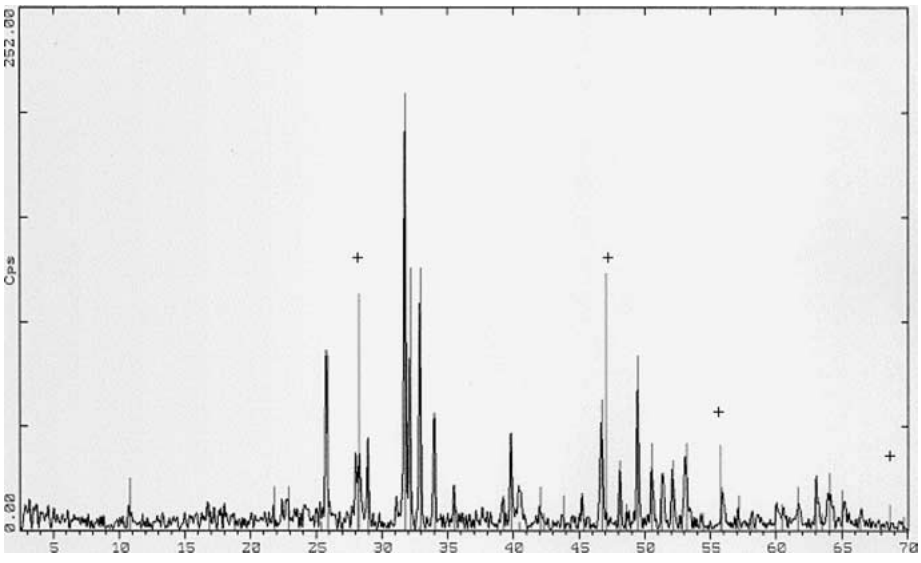

Figure 3 X-ray powder diffractogram of the sample of Fig. 1.

Figure 4 SEM micrograph of a sample prepared without silica-nanoparticles.

distributed on a substrate identified to be silica gel. The corresponding EDS analysis (Fig. 2), reveals a Ca/P ratio of 1.5 and X-ray diffraction shows the phosphate phase present to be indeed HAp (Fig. 3). The absence of the *in situ*-prepared silica nanoparticles leads to completely different results, as shown in the SEM micrograph of Fig. 4, which corresponds to a Ca/EDTA/PO_4^{-3} solution, but without the silica nanopaticles, refluxed for 8 hours. Platelets are now observed, with a Ca/P ratio below 1.3 (Fig. 5), far from the desired stoichiometric figure, and with a very high content of the monetite phase (Fig. 6). It is important to recall that, according to the literature [20, 21], the stable phase for a pH below 5 is precisely monetite and thus the method proposed here, of chemically inducing the nucleation of HAp by adding silica nanoparticles, opens interesting possibilities for producing HAp outside the known ranges of temperature and pH, which have restricted, up to now, the production of novel biomaterials. The physico-chemical details of the mechanism involved, as well as the application of this approach to other systems, will be reported separately.

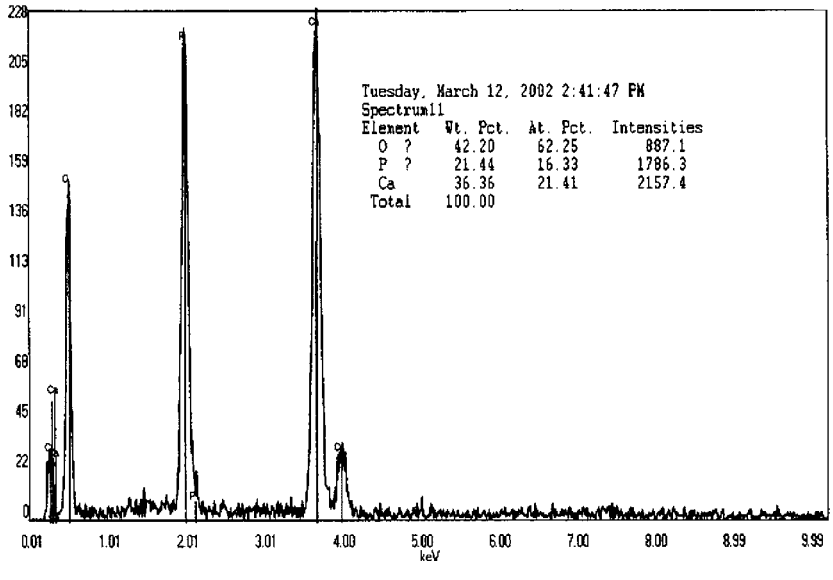

Figure 5 EDS spectrum of the sample of Fig. 4.

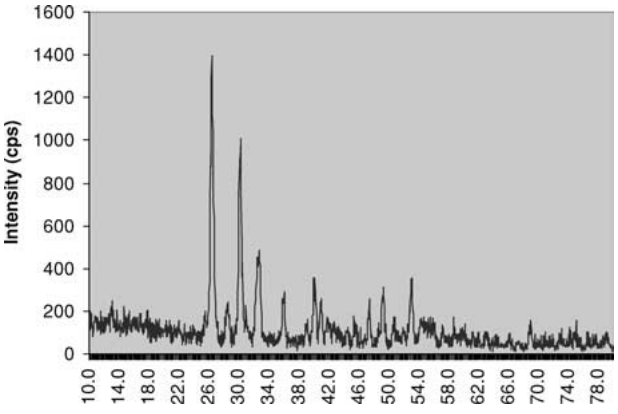

Figure 6 X-ray powder diffractogram of the sample of Fig. 6.

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