

Generation of Calcium Phosphate Nanoparticles by Laser Ablation in Ambient Conditions.

M. Boutinguiza, R. Comesaña, F. Lusquiños, A. Riveiro, J. Pou

Dpto. Física Aplicada, Universidad de Vigo, ETSI Industriales, c/ Maxwell, 36310 Vigo, Spain

mohamed@uvigo.es

Calcium phosphate-based bioceramics have been used in medicine for decades due to their excellent biocompatibility, bioactivity and osteoconductive characteristics [1]. Hydroxyapatite (HA) and related calcium phosphate ceramic materials have been widely used as implant materials because of their close similarity in composition and high biocompatibility with natural bone. In terms of biocompatibility, hydroxyapatite with the stoichiometric formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}_2)$ and a Ca/P molar ratio = 1.67 is an important bioceramic material, present in the inorganic part of the bones and teeth as nano-crystals. It seems to be a suitable ceramic material for hard tissue replacement implants and tends to form a direct bonding with the neighbouring bones [2]. It has been reported that nanocrystalline HA compared to coarse present greater biological efficacy in terms of osteoblast adhesion, proliferation and the formation of new bone on its surface [3]. On the other hand, tricalcium phosphate (β -TCP), with the formula $\text{Ca}_3(\text{PO}_4)_2$ and calcium to phosphorous ratio of 1.5 dissolves more rapidly in the body fluid than crystalline hydroxyapatite, therefore, the empty space leaved by the dissolved material can be replaced by bond tissue [4,5]. It has been reported that the use of low crystalline TCP and nanosized TCP particles improve the performance of apatitic cements [6,7] and increase the bioactivity when used in scaffolds [8].

In this work calcined fish bones, which consisted mainly of hydroxyapatite (figure 1) were used as precursor material to produce calcium phosphate nanoparticles by means of laser ablation method combined with a gas jet. As laser source, a Nd:YAG laser was employed. Morphology and composition of the obtained particles were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and conventional and high resolution transmission electron microscopy (TEM, HRTEM).

When the laser beam impinges on fish bones, its surface is exposed to thousands of high energy pulses, which cause a rapid increase of temperature, leading to material fracturing, melting and/or evaporation [9]. According to collected material, there are particles exhibiting approximately a rounded shape, which can suggest the condensation of the material in reduced fragment tending to be spherical, as can be seen in figure 2. Its shape reveals that the formation mechanism is based on a melting process. The EDX analysis showed that its composition is similar to that of calcined fish bones. The rest of the obtained particles present a reduced size, showing rounded shape, and its length is about only few nanometers, as shown in figure 3. The crystalline particles are thin enough to enable obtaining lattice fringe images. A considerable quantity of these fringes have been used to quantify the interplanar spacing by means of the fast Fourier transform, in order to compare it with those of the well known calcium phosphates (see figure 4). Results show good agreement with hydroxyapatite and β -TCP with substitutions of Mg, $(\text{Ca}, \text{Mg})_3(\text{PO}_4)_2$. The presence of Mg substituting Ca is usual in biological apatites [10]. The formation of β -TCP is promoted by the high temperature reached at the surface target [11].

In summary, the results show that nanometric particles of hydroxyapatite and β -TCP can be obtained from fish bones by combining laser ablation technique in ambient conditions and a perpendicular gas jet. The presence of β -TCP is due to the high temperature which causes the transformation of hydroxyapatite into β -TCP.

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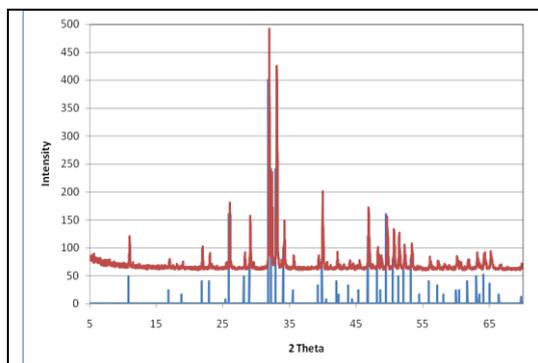


Fig. 1: XRD pattern of the used fish bones compared with stoichiometric hydroxylapatite.

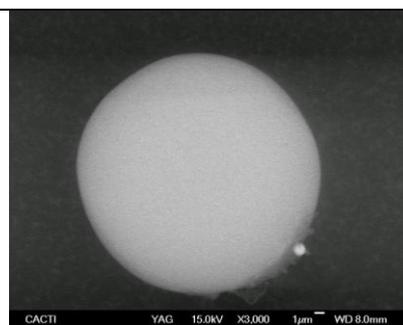


Fig. 2: particle from the interaction zone with spherical shape

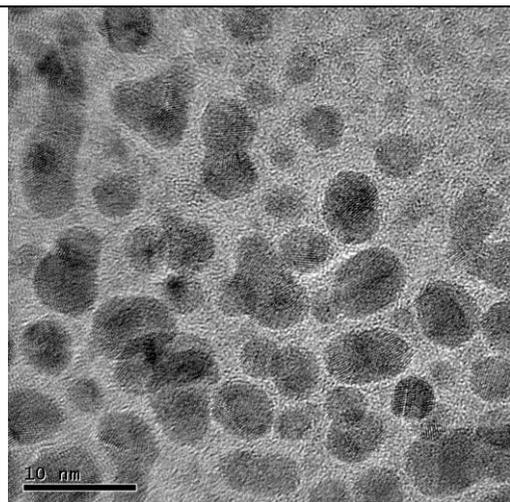


Fig. 3: HRTEM image of nanoparticles obtained from fish bones.

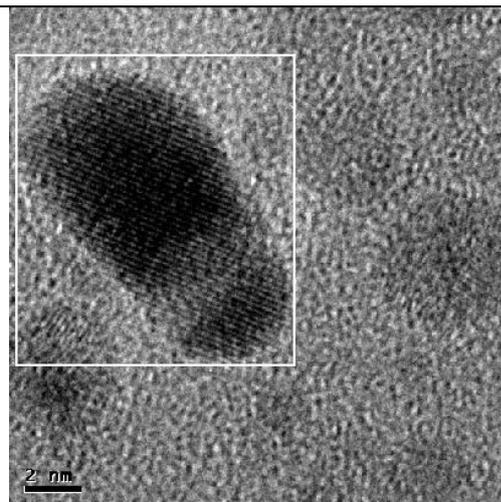


Fig. 4: HRTEM image showing the crystalline structure of a calcium phosphate nanoparticle.