Production of nanoparticles from natural and synthetic hydroxylapatite by laser ablation

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

Dpto. Física Aplicada, Universidad de Vigo, Lagoas-Marcosende,9,
36310 Vigo, SPAIN
mohamed@uvigo.es

Nanoparticles represent an important object of investigation in the field of biomaterials due to the new properties and functionalities obtainable when operating at nanoscale [1-3]. Calcium phosphate compounds in particular, such as hydroxylapatite, Ca10(PO4)6(OH)2 are getting special attention as biomaterials due their characteristics to induce bone-integration and to anchor rigidly prostheses or implants to the bone [4]. Hydroxylapatite (HA) has a special importance because of its similarities with the mineral constituents of bones and teeth, where this material is present as nanometric particles with a platelet shape [5]. On the other hand it seems that the use of β-tricalcium phosphate (β -TCP), Ca3(PO4)2 in nanosize scale and low crystallinity improves the bioactivity [6]. HA from both synthetic and natural origins is widely used in the biomaterials field.

There are different and diverse techniques for producing calcium phosphate nanoparticles, among them aqueous solutions [7], the templating technique to achieve nano-porous hydroxylapatite structure [8], or the microwave irradiation to synthesize hydroxylapatite nanostructure [9], etc. In this work we report the results of calcium phosphate nanoparticles obtained from calcined fish bones and synthetic HA using laser ablation in de-ionized water. This technique offers some advantages, such as: direct formation of nanoparticles in solutions, the absence of contamination, all particles are collected, easiness of preparation, low costs of processing, etc.

In previous work we obtained calcium phosphate micro and nanoparticles from fish bones by laser ablation in ambient conditions [10] and laser-induce fracture [11]. In the present study we report the production of β-TCP and HA nanoparticles from a natural source such as calcined fish bones and commercial synthetic HA. Pellets of calcined fish bones and commercial HA (Sigma Aldrich) were prepared as precursor material to be ablated in de-ionized water by two different lasers operating at 1064 and 1075 nm wavelength respectively. The first system used was a pulsed Nd:YAG laser delivering a maximum average power of 500 W. The laser beam was coupled to an optical fiber of 400 μm diameter and focused onto the upper surface of the target by means of 80 mm of focal length lens, where the spot diameter at normal incidence for a pulsed laser was about 0.2 mm. Other parameters were varied as follows: laser pulse width 1–3 ms, frequency 5–10 Hz, and pulse energy 2–8 J. The second laser system used was a monomode Ytterbium doped fiber laser (YDFL). This laser works in continuous wave mode delivering a maximum average power of 200 W. Its high beam quality allowed setting the irradiance range between 2 × 105 and 106 W/cm2. The laser beam was coupled to an optical fiber of 50 μm diameter using the same focusing system and processing set up than in the case of the Nd:YAG laser. Precursor material was characterized by means of X-ray diffraction (XRD) using a Siemens D-500 equipment and by X-Ray Fluorescence (XRF) taken by a Siemens SRS 3000 unit. Transmission electron microscopy (TEM), selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM) images were taken on a JOEL-JEM 210 FEG transmission electron microscope equipped with a slow digital camera scan, using an accelerating voltage of 200 kV, to reveal their crystalline. The morphology as well as the composition is described by the Scanning Electron Microscopy (SEM) using a JOEL-JSM-6700F.

The results from X-ray diffraction patterns of the material obtained from calcined fishe bones reveal that the powder is well crystallized calcium phosphate phases composed mainly by HA. Figure 1 exhibits the XRD patterns of the used fish bones and the commercial HA compared with those of stoichiometric HA (JCPDS 1993).

When the laser beam impinges on the target, 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 [12]. According to the size and morphology of the collected material, there are different kinds of particles. Some of them exhibit a rounded shape and nanometric size, as can be seen from figure 2 showing their lattice fringes. The measurement of the inter-planar spacing shows good agreement with the HA and TCP. The shape and size of these particles suggest they are obtained by melting and rapid solidification of the starting material, while the presence of TCP might be due to the crystalline transformation phase from precursor HA to β-TCP promoted by long pulse and high temperature. Other kind of particles consisted of rounded and amorphous ones with tendency to agglomeration. This kind of particles is obtained by the use of pulsed laser, which can promote the condition of thermal confinement

due to low thermal diffusivity of the starting particles together with the high pulse energy and millisecond pulses. The particles obtained from fish bones preserve the presence of some trace elements such as, Mg, K, etc. which are usual in biological apatites.

In this work nanoparticles of HA and β-TCP have been obtained by the ablation of fish bones and synthetic HA suspended in de-ionized water using pulsed as well as continuous wave laser. The use of the first one promotes the nanoparticles formation by the mechanism of evaporation and rapid condensation, while the latter one favours the melting particles formation mechanism. The presence of the β-TCP is due to the transformation of HA into β-TCP caused by the high temperature.

Acknowledgements

This work was partially supported by the European Union program POCTEP project (0330_IBEROMARE_1_P), the Spanish government (CICYT/FEDER MAT2006-10481) and by Xunta de Galicia (INCITE08PXIB303225PR, INCITE09E2R303103ES).

References

[1] W. Wang ,D. Shi, J. Lian, G. Liu, L. Wang and R. C. Ewing: Appl. Phys. Lett. **89** (2006),183106. Authors, Journal, **Issue** (Year) page.
[2]. D. Aronov and G. Rosenman: Appl. Phys. Lett. **88** (2006)163906.
[3]. H.H.K. Xu, M.D. Weir, L. Sun, S. Takagi, and L.C. Chow: J. Dent. Res. **86 (4)** (2007) 378.
[4 S.M Barinov, Y.V. Baschenko. Krajewski A (editor). Bioceramics and the human body. UK: Elsevier Science Publishers (199) 206.
[5] T. Koshino, T. Murase, T. Takagi and T. Saito. Biomat.**22** (2001) 1579.
[6] O. D. Schneider, S. Loher, T. J. Brunner, L. Uebersax, M. Simonet, R. N. Grass, H. P. Merkle, and W. J. Stark. J. Biomed. Mat. Res. B: Appl. Biomat. **84B 2** (2007) 350.
[7] L. Yubao, K. De Groot, J. De Wijn, C.P.A.T. Klein and S.V.D. Meer. J. Mater. Sci. Mater. Med. **5** (1994) 326.
[8] J. Yao, W. Tjandra, Y.Z. Chen, K.C. Tam, J. Ma and B. Soh. J. Mater. Chem. **13** (2003) 3053.
[9] J. Liu, K. Li, H. Wang, M. Zhu, H. Xu and H. Yan. Nanotechnology **16** (2005) 82.
[10] M. Boutinguiza, F. Lusquiños, R. Comesaña, A. Riveiro, F. Quintero and J. Pou. App. Surf. Sci. **254 (4)** (2007) 1264.
[11] M. Boutinguiza, F. Lusquiños, A. Riveiro, R. Comesaña and J. Pou. App. Surf. Sci. **255 (10)** (2009) 5382.
[12] Y. Chen, V. Bulatov, L. Singer, J. Stricker and I. Schechter. Anal. Bioanal. Chem. **383** (2005) 1090.

Figures

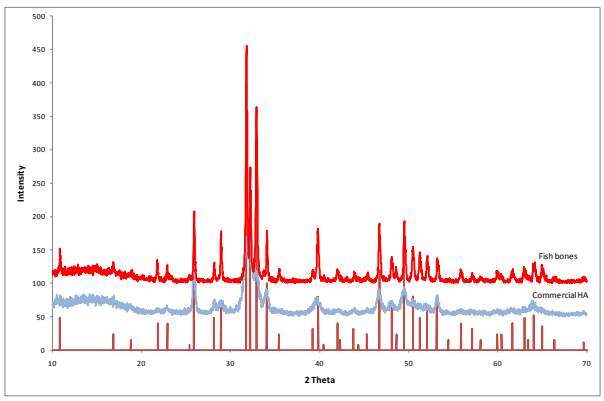

Fig. 1: *XRD patterns of calcined fish bones and commercial HA compared with stoichiometric HA.*

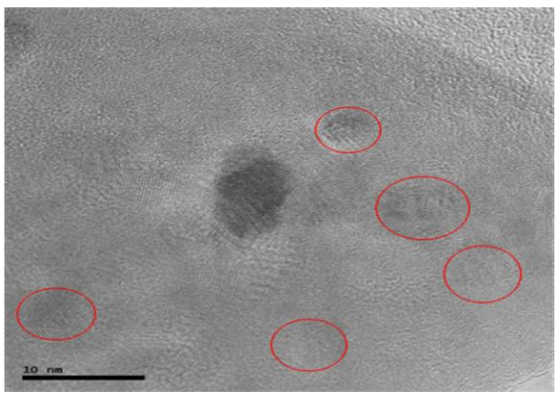

Fig. 2: *Crystalline nanoparticles obtained by laser ablation of fish bones in de-ionized water.*