

From crystalline to amorphous biomimetic (hydroxy)apatites in dependence on the preparation conditions. A HR-TEM study.

L. Bertinetti¹, S. Coluccia¹, G. Martra¹, N. Roveri², M. Sandri³ and E. Landi³

1. Dip. di Chimica IFM and NIS Center of Excellence, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy. 2. Dip. di Chimica "G. Ciamician" Università di Bologna, Via F. Selmi, 2, 40126 Bologna, Italy 3. ISTECCNR, Via Granarolo 64, 48018 Faenza, Italy.

luca.bertinetti@unito.it

Keywords: Hydroxyapatite, amorphous calcium phosphates, surface structure, biomaterials

Since long time, calcium phosphate based materials raised a relevant interest as "natural" candidates for bone repair, because of their chemical similarity to the inorganic component of this type of tissue. The intense research activity in the field highlighted that the biomimetic character of such materials can be significantly improved by tailoring size, shape and composition of the mineral particles. Furthermore, the association with organic substrates, to obtain composite materials mimicking the hierarchical organization of bone tissue appeared highly promising.

In all cases, relevant aspects of the functional behaviour of the calcium phosphate particles (ion exchange with the body fluids, dissolution/re-precipitation during the remodeling/readsorption in the host tissue) depend significantly on their structural order.

In this respect, we carried out a high resolution transmission electron microscopy (HR-TEM) investigation of a series of synthetic nano-hydroxyapatites (nano-HA), in order to highlight possible relationships between preparation methods and structural features.

Basically, nano-HA were produced by dropping a solution of H_3PO_4 in a suspension of $Ca(OH)_2$. When the precipitate was matured overnight in contact with the mother solution, platelet-like particles, $10 \times 30 \times 60 \text{ nm}^3$ in size, with large basal planes parallel to the c-axis were obtained (Fig. 1A). Such particles exhibited a crystalline structure from the core up to their surfaces. As for these latter, terminations of the (001) type appeared almost atomically flat, whereas those of the (100) type were more irregular.

By withdrawing the precipitate from the mother solution after 1h of maturation, nanoparticles with comparable size, crystalline in the bulk, but covered by a continuous, 1-2 nm thick amorphous layer were produced (Fig. 1B). However a small fraction of the materials exhibits mainly amorphous features. The precipitation in the presence of Mg^{2+} ions (molar cationic ratio in the solid: $Ca^{2+}:Mg^{2+}=92:8$) produced particles with very features (Fig. 1C) appeared to slightly promote the formation of the amorphous phase.

Additionally, an amorphous layer 1-2 nm thick was observed also for nano-HA precipitated and matured in the presence of aminoacids (either apolar or polar), which were found to significantly affect the aspect ratio of the HA nanoparticles and to promote a head-tail self assembly (Fig. 1D' and D'').

The synthesis of nano-HA in presence of collagen resulted in the nucleation of the mineral phase directly on the organic fibres. Part of the material contained crystalline platelet-like HA particles ca. 5-10 nm wide and up to 50 nm long (Fig. 1E), with the crystallographic b-axis perpendicular to the collagen fibre axis, whereas the rest was constituted by very small HA crystalline domains (2-5 nm in size) joined through an amorphous calcium phosphate grain boundaries. Conversely, in the case of Mg containing nanocomposite, the nucleation of the mineral phase completely evolved in the growth of

particles without any structural order (as confirmed by autocorrelation function analysis of UHR images), spherical in shape and significantly larger in size (40-100 nm) (Fig. 1F).

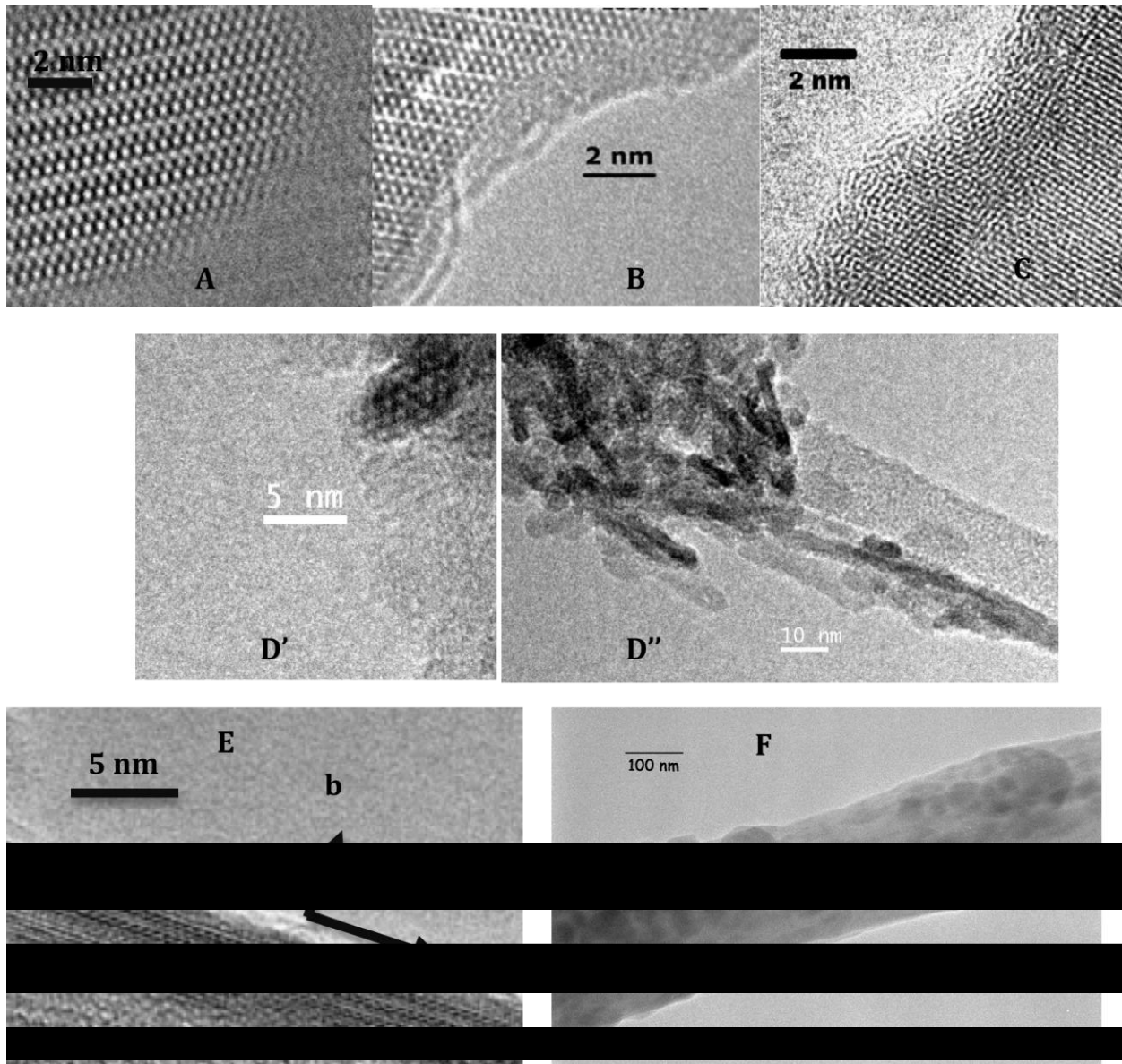


Figure 1. Nano-HA with different structural/compositional features: A) pure Calcium nano-HA fully crystalline and B) bulk crystalline with amorphous surfaces; C) Mg containing nano-HA; D' and D'') respectively top and side view of pure nano-HA synthesized in presence of polar amino-acids; E) pure Calcium nano-HA nucleated and grown on collagen fibres; F) Mg containing nano-HA nucleated and grown on collagen fibres.