Highlights

Other Materials —2017

Fe-Doping-Induced Magnetism in Nano-Hydroxyapatites

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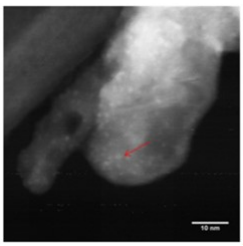

Fig. 1: STEM picture of FeHA. In picture brighter spots are highlighted by a red arrow.

We report on the production and characterization of iron-doped hydroxyapatite (HA) nanoparticles (NPs) endowed with different magnetic properties, generated by a precise setting of Fe^{2+} and Fe^{3+} ions. We found by ICP-OES spectrometry and X-ray absorption spectroscopy that: (i) Fe^{2+} substitutes calcium in the more crystalline regions and (ii) Fe^{3+} is placed as an unstructured ion in areas of the NPs with less structural restraint in the case of Fe^{2+}-doped HA (FeHA2) and Fe^{3+}-doped HA (FeHA3), or in substitution for Ca^{2+} in the apatite lattice in the case of $Fe^{2+/3+}$-doped HA (FeHA). The structure of FeHA showed a higher degree of medium-range order, evidenced by EXAFS spectra, that is probably due to Fe^{3+} ions arranged with a higher degree of order with respect to FeHA2 and FeHA3. The areas that might generate this EXAFS signal are visible by STEM as subnanometer bright spots inside FeHA NPs (Fig. 1).

FeHA NPs are rendered superparamagnetic (Fig. 2A) as a result of the formation of small amounts of a secondary iron oxide phase (maghemite crystallites on an individual HA crystallite) (Fig. 3). The presence of iron ions inside the HA NPs led to the formation of a paramagnetic-like phase down to low temperature, as evidenced by the upturn at low temperature in the magnetization curve for magnetic fields larger than 10 KOe (Fig. 2B) and by the Mössbauer analysis.

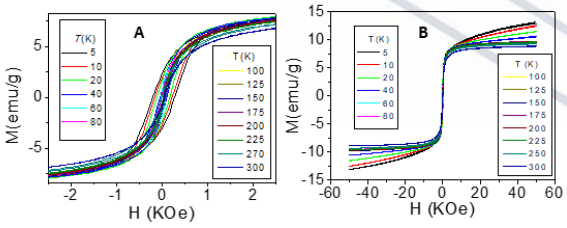

Fig. 2: (A) Enlarged view of FeHA hysteresis loops; (B) Magnetization versus magnetic field isotherms of FeHA, in the field range ± 50 KOe.

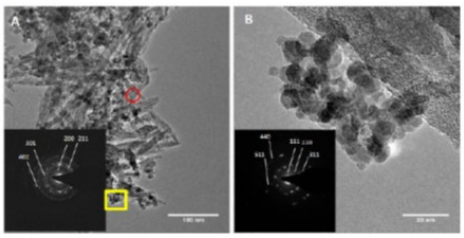

Fig. 3: TEM images collected on FeHA NPs, revealing the presence of the two different phase (A) iron -doped HA and (B) maghemite; SAED patterns collected in the red circle and in the yellow box are reported in the respective inserts.

Notably, an interacting superparamagnetic behavior due to the occurrence of dipolar interactions between segregated maghemite NPs with a saturation magnetization as high as 130 emu/(g of Fe) at room temperature, much higher than those found for superparamagnetic iron oxide NPs (SPIONs), was observed in FeHA, probably due to an unusual disposition of iron atoms. This result is very interesting not only for its implications in nanomagnetism fundamentals but also from the perspective of developing high-performance superparamagnetic NP probe systems for bioapplications in the theranostic field, considering the intrinsic biological characteristic of hydroxyapatite.