Europium and Terbium doped apatite obtained by hydrothermal transformation of biogenic calcium carbonate from oyster shells

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Seashell wastes from aquaculture and canning industries represent an important environmental issue nowadays [1]. Shells are made of calcium carbonate ($CaCO_3$) with a low content of proteins and polysaccharides (1-5 wt.%). The valorization of this waste by using it as a raw material for the production of calcium phosphates may have a positive impact both environmental and economic, thus contributing to the sustainability of this important sector. In some biomedical industries, there is a growing demand for calcium phosphate (apatite) crystals including nanosized, micron-sized, and larger sizes. This work is devoted to producing functional apatite nanocrystals, eg. doped with luminescent lanthanide (Ln^{3+}) ions [2,3], using oyster shells (Mg-calcite, 5 wt.% Mg) from the species *Crassostrea gigas* as a Ca source. Experiments were performed by a one-pot hydrothermal method using KH_2PO_4 as a P reagent, a P/$CaCO_3$ ratio of 0.6 (stoichiometric respect to hydroxyapatite), and either Eu^{3+} or Tb^{3+} (10 and 20 mM). Characterization by XRD, FTIR, Raman, and ICP revealed the full transformation of biogenic $CaCO_3$ particles into doped apatite. It was obtained at 160 ºC with (Ca+Ln)/P ratios 1.72 and 1.68 when adding Eu^{3+} and Tb^{3+} (10 mM) and 1.88 and 1.99 when the lanthanide concentration in the solution increased to 20 mM. In both cases, nanocrystals displayed needle- or plate-like morphologies and polydisperse size distribution. Luminescence characterization of the nanoparticles showed different luminescence spectra depending on the doping ion. They displayed excitation and emission wavelengths of 395nm and 616 nm for the Eu^{3+}-, and 372 and 543 nm for the Tb^{3+}-doped samples. The relative luminescence intensities correlated well with their Ln^{3+} content while luminescence lifetimes (up to 1600 µs) were higher for Tb^{3+}-doped apatites. Overall, the nanoparticles showed notable luminescent behavior and could find application as luminescent probes for bioimaging or nanophosphors for the electronic industry.
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