Microwave assisted synthesis of Poly (acrylic acid) functionalised europium doped calcium hydroxyapatite and fluoroapatite nanospindles for biomedical applications

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Nanoparticles are attracting interest in nanomedicine not only due to their potential medical applications but also because they enable analyses and therapies that cannot be performed otherwise [1]. The clinical applications of nanoparticles range from optical biolabels and contrast agents for magnetic resonance imaging to carriers for drug and gene delivery for disease therapy. All these applications require uniform nanoparticles with controlled size, shape, composition, surface chemistry and other physicochemical properties. Calcium hydroxyapatite has attracted much research attention due to their high biocompatibility and good biodegradability [2]. This is caused by the fact that calcium phosphate is the inorganic mineral of human bone and teeth [3]. However, dispersions of calcium phosphate nanoparticles tend to agglomerate and sediment [4], hindering any possible biomedical application. A further functionalization process is thus required in order to achieve colloidal stability.

Europium-doped calcium hydroxyapatite and fluoroapatite nanophosphors functionalised with poly acryl acid (PAA) have been synthesised though a microwave-assisted hydrothermal method from aqueous basic solutions containing calcium nitrate, sodium phosphate monobasic and PAA. In both cases a spindle-like morphology was obtained, resulting from an aggregation process of smaller units which gave rise to high surface area particles. The size of the nanospindles was 191 (32) x 40 (5) nm for calcium hydroxyapatite and 152 (24) x 38 (6) nm for calcium fluoroapatite. This is the first time such a spindle morphology is reported for this system. The luminescent nanoparticles show the typical red luminescence of $Eu3^{+}$. Luminescence quantum yield measurements of both europium doped calcium hydroxyapatite and calcium fluoroapatite samples indicate that the fluoroapatite particles are more efficient than the hydroxyapatite, due to the presence of OH- quenchers in the latter. The nanophosphors show negligible toxicity for cells, although the hydroxyapatite nanophosphors were slightly more biocompatible than the fluoroapatite particles. Both PAA-functionalised nanophosphors showed a very high (up to several weeks) colloidal stability in MES at pH 6.5, which is a commonly-used buffer for physiological media. All these features make both kinds of apatite-based nanoparticles suitable for biomedical applications.

References

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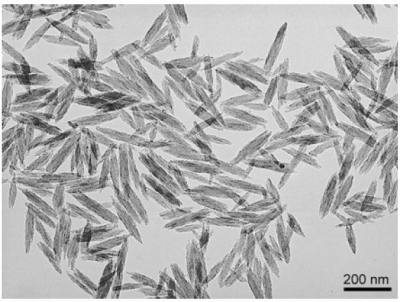

Figure 1: TEM micrograph of the 2% Eu doped calcium hydroxyapatite nanophosphors synthesized and functionalised with PAA.

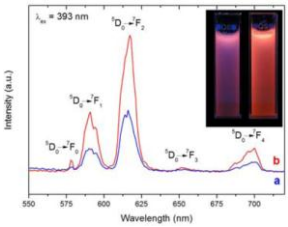

Figure 2: Emission spectra (λexc 393 nm) of aqueous suspensions of 2% doped calcium hydroxyapatite (a, blue line) and fluoroapatite (b, red line). The spectra were carried out with the same nanophosphors concentration. The image shows the luminescence of suspensions of 2% Eu calcium hydroxyapatite (left) and fluoroapatite (right) with the same nanoparticle concentration when irradiated with UV light.