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Photoluminescence studies of functionalized lanthanide doped hydroxyapatite particles

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Luminescence is one of the most remarkable properties of lanthanide ions (Ln^{3+}). Ln^{3+} luminescence is highly utilized in a wide range of applications owing to the advantages they possess. Doping Ln^{3+} into inorganic material is one strategy to incorporate luminescence into non-luminescent inorganic materials. Hydroxyapatite (HAp) is one of the most important inorganic materials in bones and teeth. HAps are used in many applications including bioimaging, tissue engineering and water purification. Useful properties can be incorporated into HAp by fabricating HAp with desired dopants. Ln^{3+} have similar radii to Ca^{2+}; hence, Ln^{3+} can be doped into HAp to achieve the luminescence. Europium and terbium ions are most commonly used lanthanides in optical probes. Therefore, in this study, europium and terbium doped hydroxyapatite particles (EuTb-HAp) were investigated for their luminescence. Owing to LaPorte forbidden nature of *f-f* transitions, EuTb-HAp did not show prominent emission. Hence, EuTb-HAp were functionalized with dipicolinic acid (DPA) to increase luminescence using antenna effect. The primary goal of this research project is to synthesize HAp doped with Ln^{3+} and functionalized with DPA, which can be utilized as a luminescent probe. Well-crystallized HAp doped with both Eu^{3+} and Tb^{3+} have been successfully synthesized by coprecipitation method, maintaining the $[Eu^{3+}] = [Tb^{3+}]$ and ratios of Ln^{3+} to Ca^{2+} at 20 % and (Ca+ Ln)/ P at 1.67. Particles were functionalized *in situ* with DPA to achieve better luminescence. Synthesized EuTb-DPA-HAp were characterized by UV-absorbance and luminescence emission. Characterizations showed successful doping of both Eu^{3+} and Tb^{3+}, as well as the incorporation of DPA into HAp matrix. The addition of DPA into EuTb-HAp caused a great enhancement in luminescence emission when excited at 272 nm wavelength, which corresponds to the maximum absorbance wavelength of DPA. Synthesized EuTb-DPA-HAp showed characteristic Eu^{3+} and Tb^{3+} peaks at 490 nm, 545 nm, 590 nm and 620 nm. Tb3+ peaks were more prominent masking emission peaks from Eu3+ due to less energy transfer to Eu^{3+}. However, when the less intensed peaks at 589 nm and 620 nm are expanded, a clear splitting can be seen indicating emission peaks form both Tb and Eu. Finally, our study showed that the lanthanides can be easily doped to the HAp matrix and efficient transfer of energy from DPA to lanthanide ions take place within the HAp matrix.

Keywords: Lanthanide ions, hydroxyapatite, dipicolinic acid, EuTb-DPA-HAp, luminescence

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