Synthesis and characterization of blue-emitting core-shell nanoscintillators for X-ray induced photodynamic therapy (X-PDT) applications

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Scintillating nanoparticles (ScNPs) have the potential to be combined with photosensitizers (PS) for application in X-ray–activated photodynamic therapy (X-PDT). However, most PS with high reactive oxygen species (ROS) generation absorb in the blue region [1], whereas few ScNPs exhibit strong scintillation in this spectral range [2]. Our group synthesized and characterized SrF_2:Eu nanoparticles that emit in both the blue region, due to Eu^{2+}, and the red region, corresponding to the characteristic emission of Eu^{3+} [3]. The literature indicates that the europium valence state depends on its position within the crystal lattice [4], suggesting that Eu^{2+} may be located in the core while Eu^{3+} is predominantly present at the surface. Based on this rationale, and aiming to promote the reduction of Eu^{3+} to Eu^{2+} in order to enhance blue emission, SrF_2 shells were grown on the SrF_2:Eu nanoparticles with different thicknesses.

SrF_2:Eu nanoparticles with different dopant concentrations (2.5%, 5%, 7.5%, and 10%) were synthesized by the co-precipitation method at 40 °C, using $Sr(NO_3)_2$, $EuCl_3$, and NH_4F as precursors. The SrF_2:Eu nanoparticles with 5% dopant content were employed as cores for the growth of SrF_2 shells with different thicknesses, which were obtained by varying the SrF_2 concentration. The core–shell molar ratios used (in mmol) were 1:0.1, 1:0.25, 1:0.5, 1:0.75, and 1:1. The materials were characterized by dynamic light scattering (DLS), zeta potential measurements, transmission electron microscopy (TEM), X-ray diffraction (XRD), photoluminescence (PL) and radioluminescence (RL).

TEM images of the cores with different dopant concentrations showed particle sizes of approximately 20 nm. The largest nanoparticles obtained exhibited an average size of 45 ± 14 nm and corresponded to core–shell nanoparticles with a 1:0.75 core-to-shell ratio and a reaction time of 28 h, suggesting the existence of a saturation ratio beyond which separate SrF_2 nanoparticles begin to form. Radioluminescence analysis revealed that the strongest blue emission was observed for the core–shell nanoparticles with a 1:1 ratio and a reaction time of 42 h, for which the Eu^{2+}/Eu^{3+} radioluminescence area ratio reached 1.98, whereas this ratio was 0.48 for the 5% doped core nanoparticles. Debye–Scherrer analysis of the XRD patterns indicated a decrease in crystallite size for the SrF_2:Eu samples with increasing dopant concentration, while the SrF_2:Eu@SrF_2 nanoparticles exhibited an increase in crystallite size with increasing SrF_2 molar ratio used for the shell.

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