$LiCaAlF_6$:Eu Nanoscintillators for X-Ray Triggered Release of Nitric Oxide

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X-ray–activated scintillating nanoparticles (NPs) have attracted considerable interest for advanced applications that harness their ability to convert ionizing radiation into optical emission. In this work, we report the synthesis, structural and radioluminescent optimization, and surface functionalization of europium-doped $LiCaAlF_6$ nanoparticles engineered as efficient nanoscintillators with tunable emission properties.

$LiCaAlF_6$:Eu NPs were synthesized via a hydrothermal route with systematic variation of reaction time, temperature, and polyvinylpyrrolidone (PVP) concentration. X-ray diffraction confirmed the formation of phase-pure hexagonal $LiCaAlF_6$, while transmission electron microscopy revealed a strong dependence of particle size and morphology on synthesis conditions. The presence of PVP was crucial in suppressing excessive crystal growth and agglomeration, yielding well-dispersed NPs with average diameters below 130 nm (Fig. 1a).

Radioluminescence (RL) measurements under X-ray excitation demonstrated intense emission dominated by the Eu^{2+} 5d–4f transition at ~370 nm, with a minor Eu^{3+} contribution in the visible range [1]. The RL intensity was highly sensitive to synthesis parameters, with the sample prepared at 190 °C for 4 h with 10 µM PVP exhibiting the highest integrated emission. This enhancement is attributed to reduced particle size, improved crystallinity, and surface defect passivation.

The optimized nanoscintillators were functionalized with nitrofurantoin (NTF), a molecule capable of releasing nitric oxide (NO) upon photoactivation. A favorable spectral overlap between RL emission and NTF absorption enabled efficient X-ray activation (Fig. 1b), as confirmed by electron spin resonance spectroscopy using the Fe-DETC spin-trapping system. Maximum NO release was observed for nanoparticles with four deposition layers (Fig. 1c).

These results demonstrate that $LiCaAlF_6$:Eu nanoparticles are efficient and tunable scintillators with potential applications in X-ray–activated emission processes and external activation schemes, highlighting their relevance for future advancements in scintillating materials.

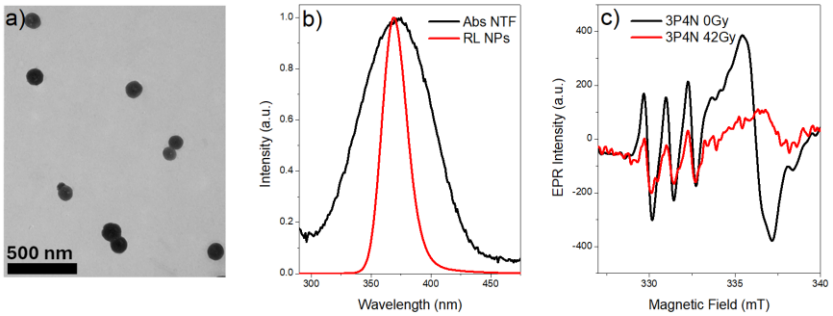

Figure 1. *(a) TEM image of optimized $LiCaAlF_6$:Eu nanoscintillators (190 °C, 4 h, 10 µM PVP). (b) Absorbance spectrum of NTF and RL emission of $LiCaAlF_6$:Eu, showing spectral overlap. (c) ESR spectra of $LiCaAlF_6$:Eu@NTF with four depositions under irradiated and non-irradiated conditions, demonstrating X-ray–triggered NO release.*

1. T. Yanagida, Y. Fujimoto, K. Watanabe, K. Fukuda, "Dosimeter properties of Ce and Eu doped LiCaAlF6", Radiat Meas 71 (2014) 148–152.

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