Spectral-kinetic properties of YF$_3$-CeF$_3$: Eu$^{3+}$/Tb$^{3+}$ nanoparticles as possible sensitizers of PDT dyes

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Abstract. Optical properties of crystalline CeF$_3$-YF$_3$ nanoparticles doped with Eu$^{3+}$ or Tb$^{3+}$ ions were studied. The energy transfer coefficients from Ce$^{3+}$ to the doping ions were estimated. As well as this, conjugation of nanoparticles and dye molecules using polyethyleneimine was tested. The energy transfer from the nanoparticles to dye molecules was studied.

Hybrid Photodynamic therapy (HPDT) technique have been extensively developing over recent years in an attempt to overcome the limitation of the traditional photodynamic therapy (PDT). This technique implies that a dye used in PTD can be conjugated with a scintillating nanoparticle (NP), which will convert ionizing radiation energy into excitation of a dye and ROS generation [12]. Utilization of down-converting radioluminescent or scintillating NPs is a that method implies use of the NPs that emit ultraviolet or visible light upon excitation by highly penetrating ionizing radiation [2]. The goal of the current study is to determine optimal chemical composition of the nanoparticles to be used in conjunction with a photosensitizer dye, study the energy transfer processes in the nanoparticles and conduct initial experiments of the energy transfer between nanoparticles and photosensitizer. The CeF$_3$-Y$_{1-x}$Tb$_x$F$_3$ nanoparticles with x = 0.1%, 1%, 5%, 10%, 15% and 20 and Y$_{0.45}$Ce$_{0.5}$Eu$_{0.05}$F$_3$ nanoparticles were synthesized via a co-precipitation technique. After the initial reaction the solution was treated with microwave radiation for 180 minutes, then the residue was washed several times. The washing procedure consisted of consecutive centrifuging and suspension with an ultrasonic bath. The morphology of the samples was characterised with transmitting electron microscopy. Images presented in figure 1 demonstrate that the size of the particles is 10-15 nm and that show high level of crystallinity. To study the energy transfer processes in the nanoparticles the luminescence decay kinetics were recorded. The luminescence decay curves in of the Ce$^{3+}$ ions at 335 nm under 299 nm excitation are presented in figure 2. The energy transfer coefficient in case of the sample doped with Eu$^{3+}$ ions is 62% and in case of the Tb$^{3+}$ doped samples reaches 86% at 20% doping level. The conjugates of nanoparticles and Radachlorin molecules were studied. The luminescence spectra as well as luminescence decay curves of the Tb$^{3+}$ ions at 541nm were recorded under 299 nm excitation. The results are presented in figure 3.

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Fig. 1. TEM images of the (a) Y\textsubscript{0.45}Ce\textsubscript{0.5}Tb\textsubscript{0.05}F\textsubscript{3} nanoparticles (b) highlighted area.

Fig. 2. Room temperature decay curves of the CeF\textsubscript{3}-YF\textsubscript{3} nanoparticles doped with (a) Eu\textsuperscript{3+} (5%), (b) various amounts of Tb\textsuperscript{3+} ions under 299 nm excitation.

Fig. 3. (a) Luminescence spectrum of the Y\textsubscript{0.4}Ce\textsubscript{0.5}Tb\textsubscript{0.1}F\textsubscript{3} colloid with Radachlorin (b) Luminescence decay curves of the Y\textsubscript{0.4}Ce\textsubscript{0.5}Tb\textsubscript{0.1}F\textsubscript{3} colloid with various concentrations of Radachlorin.

Radachlorin was added to the CeF\textsubscript{3}-Y\textsubscript{0.5}Tb\textsubscript{0.1}F\textsubscript{3} nanoparticles in a stepwise manner and then water was added to the obtained conjugates. The results demonstrate formation of the stable conjugates. The energy transfer coefficient from nanoparticles to dye molecules was 38%.

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References