Spectral properties of hybrid associates of colloidal quantum dots $Zn_{0.5}Cd_{0.5}S$, europium tenoyltrifluoroacetonate and methylene blue

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Abstract. Hybrid associates formed from colloidal $Zn_{0.5}Cd_{0.5}S$ quantum dots, passivated with thioglycolic acid, europium tenoyltrioteracetonate and methylene blue molecules, absorption, luminescence, IR and time-resolved spectroscopy technique are studied. The shift of the IR absorption bands of COO^- and C=O groups of thioglycolic acid and europium thenoyltrifluoroacetonate has been detected. An increase in the efficiency of excitation of europium luminescence and a simultaneous increase lifetime of its luminescence upon adsorption on $Zn_{0.5}Cd_{0.5}S$ quantum dots were found. Addition of methylene blue (thionine) molecules leads to quenching of the trap state luminescence of $Zn_{0.5}Cd_{0.5}S$ and intracentric luminescence of Eu^{3+}. A conclusion about the adsorption of Eu^{3+} on the surface of $Zn_{0.5}Cd_{0.5}S$ quantum dots and the nonradiative energy transfer to methylene blue molecules was made.

Semiconductor crystals and dielectrics, doped with rare earth element (RRE), find extensive applications as materials for solid-state lasers, fiber amplifiers, biolables, solar cells, etc. Quantum dots (QDs) doped with RRE, whose own optical and electronic properties have a size dependence, have considerable interest. Among them are QDs doped with europium ions. An additional modification of the optical properties can be achieved by conjugating of doped quantum dots with molecules of organic dyes.

The fig. 1 shows the luminescence spectra of QDs of $Zn_{0.5}Cd_{0.5}S$/TGA in ethanol solution, and also their mixtures with europium tetrafluoroacetonate (Eu^{3+}:TTA), introduced at the stage of QDs crystallization. The luminescence in band with a maximum at 520 nm occurs with participation of trap states. In the luminescence spectrum of Eu^{3+}: TTA the peaks are present: at 592 nm, 615 nm, 653 nm and 702 nm - transitions between terms $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$, respectively.

At introducing of Eu^{3+}:TTA into a colloidal solution with emerging QDs, the changes in luminescence properties were observed: - with increasing of QDs concentration, the luminescence intensity of Eu^{3+} in all bands initially increases by 5 times, and then decreases; - with increasing of concentration of Eu^{3+}:TTA, the intensity of trap state luminescence decreases strongly, and the luminescence lifetime decreases; - at increasing

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of QDs concentration to 20%, luminescence decay in the Eu^{3+} band slows down; - the intensity of the emission Eu^{3+} grows at the initial point of decay of its luminescence, i.e. the effectiveness of its excitation is growing.

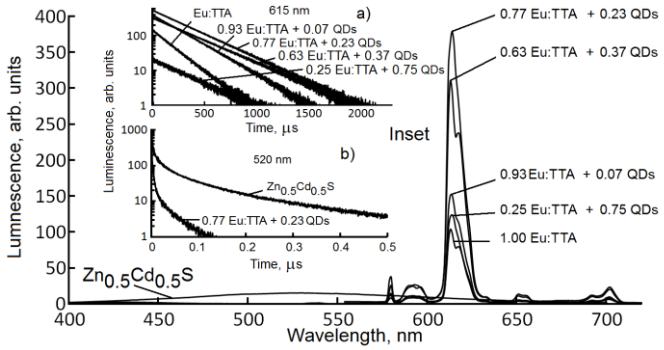

Fig. 1. Spectra of luminescence of $Zn_{0.5}Cd_{0.5}S$/TGA+Eu^{3+}:TTA. In the insert is decay of luminescence of $Zn_{0.5}Cd_{0.5}S$/TGA and Eu^{3+}:TTA.

It can be concluded that an association of QDs and Eu^{3+}: TTA is observed. Two types of similar associates are possible: i - some TTA molecules are replaced by TGA molecules and a carboxylate complex is formed. The structure of such a complex can be represented in the form $Zn_{0.5}Cd_{0.5}S$/TGA/Eu^{3+}. ii - Eu^{3+} is adsorbed to QDs and integrated into the near-surface layer of QDs. The structure of $Zn_{0.5}Cd_{0.5}S$/$Zn_{0.5}Cd_{0.5}S$:Eu^{3+}:TTA (TGA), passivated by TGA and TTA molecules, is formed.

According to the IR absorption spectra, it was established on the basis of insignificant shifts in the absorption bands of the carboxyl group of TGA and the carbonyl group of TTA that the formation of $Zn_{0.5}Cd_{0.5}S$/$Zn_{0.5}Cd_{0.5}S$: Eu^{3+}:TTA (TGA), i.e. doping of QDs with Eu^{3+} ions.

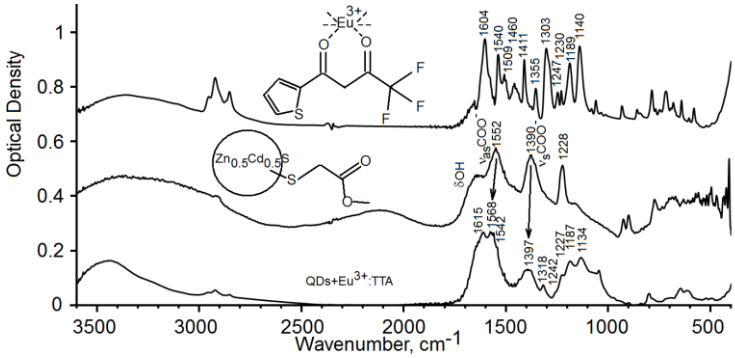

Fig. 2. FTIR spectra and structures of the investigated samples.

The conjugation of QDs of $Zn_{0.5}Cd_{0.5}S$/$Zn_{0.5}Cd_{0.5}S$:Eu^{3+}:TTA (TGA), with molecules of methylene blue (thionine) leads to quenching of trap state luminescence and intracentric luminescence and rise up of luminescence of the dye. At the same time, the luminescence lifetime in the bands of trap state luminescence and intracentric luminescence is reduced. A conclusion about the transfer of energy from the center of recombination luminescence and from the intracentral luminescence of Eu^{3+} is drawn.

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