Effect of conjugation with oligonucleotides on the photoluminescence of the AgInS₂/ZnS quantum dots L. Borkovska^{1*}, T. Stara¹, K. Kozoriz¹, A. Rachkov² and J.-L. Doualan³

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Objectives

The **AgInS**₂/**ZnS** core shell quantum dots (QDs) are characterized by high absorption coefficient and intense photoluminescence (PL) in the visible spectral range [1]. These objects also show a reduced toxicity. These cause high perspectives of their application in **bio-imaging** and **bio-sensing** [2].

The **aim of the work** was to study the influence of conjugation with **80-basic oligonucleotide 80-bcr-abl** on the PL of the AgInS₂/ZnS QDs. This is important for development of the methods for diagnostics of genetic and infectious diseases of people. This oligonucleotide reproduces the nucleotide sequence of the mRNA region of the hybrid gene bcr-abl. A protein product of this gene causes the development of pH'-positive forms of leukemia.



Room temperature PL spectra of the QDs showed a wide band in the orange-red spectral region peaked at ~ 587 nm and 627 nm with a Stokes shift of 0.7 eV and 0.85 eV for glutathione- and MAA-stabilized QDs, respectively. The PL was ascribed to carrier recombination via the levels of intrinsic defects inside or at the surface of QDs.

In the PLE spectra of glutathione capped QDs, an absorption edge shifted to longer wavelengths as the detection wavelength increased within the PL band. The shift was not observed for MAAcapped QDs. This effect was ascribed to variation of QDs in size.



The PL relaxation times determined from the PL decay curves increased from ~100 ns to 880 ns with the increase of detection wavelength within the PL band. These changes were found for both MAA- and glutathione-stabilized QDs and explained by contribution of defects of different types in the PL spectrum.

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Experimental details

The **QDs were synthesized** in mild conditions in aqueous solutions and stabilized by mercaptoacetic acid (MAA) or glutathione. The glutathione capped QDs were separated in size and only one set of the QDs of larger size was studied.

Purified aqueous solution of the QDs was mixed with citrate buffer solution of pH=7.2 and a solution of 80-bcr-abl oligonucleotides.

The **photoluminescence** (PL) spectra were studied at room temperature under excitation by a light of 409 nm LED. The PL excitation (PLE) spectra were excited by a light of xenon-lamp passed through a grating monochromator. The relaxation of the PL intensity was studied under excitation by a pulse laser of 410 nm.



The **PL intensity** and PL **relaxation times** of the QDs **increased** due to attachment of oligonucleotides. For glutathione capped QDs, the PL intensity increased almost twice and the PL band shifted to shorter wavelengths on ~10 nm, while for MAA- capped QDs the PL intensity increase was much smaller and no spectral shift of PL band was found. The **increase of PL relaxation times** was observed for all detection wavelengths and varied from 10 % to 2 times. This effect was ascribed to passivation of QD surface defects by oligonucleotides and improvement of QD solubility in buffer solution. The effect is supposed to be more pronounced for the QDs of smaller size.

Conclusions

The effect of conjugation with 80-bcr-abl oligonucleotides on the defect-related photoluminescence of the $AgInS_2/ZnS$ core-shell QDs was investigated.

The **conjugation influenced the PL characteristics** of the QDs and resulted in: (1) the increase of the PL intensity,

- (2) the shift of the PL band to shorter wavelengths and
- (3) the increase of the PL relaxation times.

The **value** of PL changes depends on the type of stabilizing ligands (MAA or glutathione) and variation of QDs in sizes.

The largest changes of PL characteristics were observed for glutathione stabilized QDs not separated in sizes.

References

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