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Modification of optical properties at bioconjugation of core-shell CdSe/ZnS quantum dots

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Abstract. This paper presents the results of photoluminescence study of core-shell CdSe/ZnS quantum dots (QDs) with radiative interface states in nonconjugated and bioconjugated conditions. PL spectra of nonconjugated QDs are characterized by a superposition of PL bands related to exciton emission in CdSe cores (2.36 eV) and to electron-hole emission via interface states (2.00, 2.75 and 3.04 eV) at the CdSe/ZnS or ZnS/polymer interfaces. The CdSe/ZnS QDs with emission at 525 nm have been conjugated with bio-molecules - mouse ovarian cancer (OC 125) antibodies. It is revealed that PL spectrum of bioconjugated QDs has changed dramatically with essential decreasing of the hot electron-hole recombination flow via interface states. This effect is explained on the base of the model deals with re-charging of QD interface states at the bioconjugation with OC125 antibodies. The nature of interface states and their changes at the QD aging process have been discussed as well.

1. Introduction
Semiconductor core/shell quantum dots (QDs) have unique optical properties such as QD-size tunable photoluminescence (PL) with narrow emission bandwidths and sufficiently high quantum efficiency. The most popular QDs are core/shell CdSe/ZnS QDs that is characterized by the high photoluminescence quantum yield. Their emission can be changed with the variation of CdSe core size due to the quantum confinement effect [1-3]. The ability to cover these QDs with biomolecules is a critical step in producing the efficient bio-luminescent markers [2,4,5]. Spectroscopic confirmation of bioconjugation with the detection not only the variation of PL intensity but also the spectral transformation of emission spectra, the changes in peak positions and in a band full width at half maximum (FWHM) is highly important. This paper presents the results of PL analysis of CdSe/ZnS core/shell QDs nonconjugated and bioconjugated to bio-molecules – the mouse ovarian cancer (OC 125) antibodies (mab).

2. Experimental details
Commercially available core-shell CdSe/ZnS QDs covered with polymer are used in a form of colloidal particles diluted in a phosphate buffer (PBS) with a 1:200 volumetric ratio. Studied QDs are characterized by the color emission with the maxima at 525 nm (2.36 eV). The part of CdSe/ZnS QDs...
has been bioconjugated (named 525P) to the mouse ovarian cancer (OC 125) antibodies using the commercially available 525 nm QD conjugation kit [6]. The conjugation reaction is based on the efficient coupling of thiols that present in reduced antibodies, to reactive maleimide groups which exist on the QD surface after SMCC activation. The part of CdSe/ZnS QDs (525N) has been left nonconjugated and serves as a reference object. Samples of QDs (bioconjugated and nonconjugated) in the form of a 5 mm size spot were dried on a polished surface of crystalline Si substrates as described earlier in [7-11]. PL spectra were measured at 300 K and at the excitation by a He-Cd laser with a wavelength of 325 nm and a beam power of 20 mW using a PL setup described in [9, 10].

3. Experimental results and discussion

Normalized PL spectra of pure nonconjugated CdSe/ZnS QDs measured at 300K demonstrate the broad PL band in the spectral range of 1.80-3.20 eV with a main maximum at 2.69 -2.75 eV and shoulders (or small peaks) (Fig.1a).

The deconvolution procedure has been applied to the PL spectrum permitting to represent it as a superposition of four elementary PL bands with the peaks at 2.20, 2.36, 2.73 and 3.06 eV (Fig.1a, curves 1-4). The PL band with a peak at 2.36 eV is related to the emission of ground state exciton in the CdSe core. Three other PL bands with the peaks at 2.20, 2.73 and 3.06 eV need to be discussed. High energy PL bands (2.73 and 3.06 eV) can be assigned to the recombination via: i) interface states at the CdSe/ZnS interface; ii) excited states in the CdSe core or iii) states at the ZnS/polymer interface. The PL spectrum of non-conjugated CdSe/ZnS QDs has been studied earlier at a low (10K) temperature with the aim to clarify the nature of high energy PL bands [12]. The PL band related to exciton emission in the CdSe core shifted toward high energy due to the increase of CdSe optical band gap with temperature decreasing [12]. At the same time the PL bands (2.20, 2.73 and 3.06 eV) did not change their peak positions versus temperature [12]. The last fact testifies that high energy PL bands do not connect with excited states in the CdSe core. Thus these PL bands (2.20, 2.73 and 3.06 eV) can be assigned to the interface states. This conclusion has been confirmed additionally by the same position of high energy PL bands in core/shell CdSe/ZnS QDs of different core sizes [10].

Earlier it was revealed the very fast (subpicosecond) electron and hole relaxation dynamics in CdSe QDs with the rate exceeding that due to phonon emission in the bulk semiconductors [13,14]. Taking into account very fast depopulation dynamics of electron and hole quantized states in CdSe QDs it is possible to suppose that radiative states responsible for the 2.20, 2.73 and 3.06 eV PL bands are localized at the CdSe/ZnS or at ZnS/polymer interfaces (Fig.2).

The PL spectrum of CdSe/ZnS QDs bioconjugated with the mouse ovarian cancer (OC 125) antibodies has been modified dramatically (Fig.1b). At the same time the PL intensity has not changed. The PL spectrum of bio-conjugated QDs is characterized by the one Gaussian shape PL band with a narrow
full width at half maximum (90-150 meV) and the peak position of 2.36 eV at 300K (Fig.1b) related to exciton emission in the CdSe core.

Figure 2 The energy diagram of CdSe/ZnS core/shell QDs covered by polymer. Symbols $IS^+/$ and $IS^-$ present the charge of donor-like and acceptor-like interface states (IS), respectively, in nonconjugated ($IS^-$ and $IS^+$) and bioconjugated ($IS^-$ and $IS^0$) CdSe/ZnS QDs [11]. Dashed lines below IS symbols show the ways of carrier tunnelling from CdSe/ZnS interface states to the ZnS/polymer interface.

To explain presented results we use the bioconjugation model proposed in [11]. Actually it is possible to suppose that the interface states (IS), responsible for the hole trapping in nonconjugated QDs, are negatively charged acceptor-like defects (IS') [15-17]. Simultaneously, the interface states, responsible for the electron trapping in non-conjugated QDs, are positively charged donor-like defects (IS') [15-17]. The negative charge of acceptor-like interface states is due to their compensation by the electrons from donor-like interface states in nonconjugated CdSe/ZnS QDs (Fig.2). The localization of defect states at the QD interface and their attractive potentials permit them to compete in the recombination process with exciton recombination inside the CdSe core (Fig.2) [11, 18-21]. To explain the PL spectrum transformation in bioconjugated QDs the interface state re-charging was proposed in [11]. It is known that some biomolecules have a positive charge on their surface (related to $H^+$ ions) that can participate in electrostatic interaction during the bio-conjugation process with the negative charge on the QD surface. In this case follow the model presented in [11] in bioconjugated QDs the acceptor-like interface states are neutral (IS0) and cannot compete with exciton recombination inside QDs. As a result the recombination flow via interface states decreases.

Figure 3. Normalized PL spectra of nonconjugated 525 nm QDs measured at 300 K in different moments of aging in air: 1-30 days, 2-40 days, 3-90 days, 4-120 days. Numbers at the curves indicate the multiplication coefficients (x1.0, x1.8, x3.6, x16) used at the normalization of experimental PL spectra.

Earlier we have seen such type of effects in the 605 nm CdSe/ZnS QDs bioconjugated with anti human Interleukin 10 antibodies [9,11]. The variation of PL spectra at the bioconjugation was similar, but the integrated PL intensity in bioconjugated QDs increased six- or tenfold. In the case of bioconjugation of 525 nm CdSe/ZnS QDs with the mouse ovarian cancer (OC 125) antibodies the
integrated PL intensity of bioconjugated QDs did not change. The last effect can be explained by the re-absorption of light emitted by 525nm QDs in the mouse ovarian cancer (OC 125) antibodies.

The nature of interface states is not clear. It is supposed that the interface states appear at the ZnS/polymer interface in the process of polymer aging in air. To understand the interface state origin the variation of PL spectra of nonconjugated QDs at the aging in air has been studied. Fig. 3 presents the PL spectra of nonconjugated 525 nm QDs measured in the period of 30-120 days after the nonconjugated QD sample preparation (525N). As one can see two effects can be revealed from these PL spectra: i) the transformation of PL spectra and ii) PL intensity increasing. The first effect related to the intensity stimulation of 2.73 and 3.06 eV PL bands, apparently, due to appearing the corresponding interface states. It is assumed that the second effect appears owing the polymer transparency increasing for 525 nm QD emission at the aging in air of polymer covered QDs.

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