Electronic effects in CdSe/ZnS quantum dots conjugated to IL-10 antibodies

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ABSTRACT

The paper presents the study of photoluminescence (PL) and Raman scattering spectra of nonconjugated and bioconjugated CdSe/ZnS core-shell quantum dots (QDs). CdSe/ZnS QDs used are characterized by color emission with the maxima at 605 nm (2.05eV) and 655 nm (1.89 eV). The QD conjugation has been performed with biomolecules – the anti Interleukin 10 antibodies (anti IL10 mAb). PL spectra of nonconjugated QDs are characterized by one symmetric PL band related to exciton emission in the CdSe core of QDs. PL spectra of bioconjugated QDs have changed essentially: PL band shifts into high energy side and becomes asymmetric. To explain last effect the model has been proposed which assumes that the PL spectrum transformation in bioconjugated QDs is connected with the Stark effect. To confirm the existence of electric dipoles in anti IL-10 mAb the Raman scattering spectra have been investigated. The enhancement of Raman scattering is observed in bioconjugated CdSe/ZnS QDs. The last effect testifies that the IL10 antibodies are characterized, actually, by the electric dipole moment that permits them to interact with an electric field of excitation light and to provoke the surface enhanced Raman scattering (SERS) and the Stark effects in QDs..

Keywords: CdSe/ZnS quantum dots, anti Interleukin 10 antibody, bioconjugation, photoluminescence, Raman scattering

1 INTRODUCTION

The integration of nanotechnology with biomedicine is expected to produce the major advances in bioengineering, early cancer diagnostic, biosensors, therapeutic etc [1, 2]. Semiconductor core/shell CdSe/ZnS quantum dots (QDs) due to their unique optical properties and dimensional similarities to biomolecules have attracted the great attention in biomedicine during a last decade [3-5]. These QDs used as bio-luminescent markers can vary the photoluminescence (PL) intensity when coupled to different biomolecules and thus indicate the changes in the quantity of these molecules. The process of QD bioconjugation, as a rule, is accompanied by the variation of QD PL intensity mainly. The confirmation of QD bioconjugation and the study its details using the detection of PL spectrum transformation are highly important as well. Additionally it is important to look for other optical effects, such as Raman scattering, in QD bioconjugation, which could offer the important information on the structure of bioconjugated QDs along with proof of actual bioconjugation.

This paper presents the results of PL and Raman scattering analysis of CdSe/ZnS core/shell QDs with color emission at 605 and 655 nm nonconjugated and bioconjugated to biomolecules – the anti Interleukin 10 antibodies (anti IL10 mAb).

2 ESPERIMENTAL DETAILS

The commercially available core-shell CdSe/ZnS QDs covered with a PEG polymer were 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 size of 5.4 nm and 7.3 nm and by color emission with the maxima at 605 nm (2.05eV) and 655 nm (1.89 eV), respectively. The part of CdSe/ZnS QDs (605P, 655P) has been conjugated to anti Interleukin (IL10) antibodies (antihuman IL10, Rt IgG1, stock concentration of 1mg/ml, clone JES3-9D7, code RHCIL1000) using the commercially available 605 and 655 nm QD conjugation kits [6,7]. Some part of CdSe/ZnS QDs (605N, 655N) 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 [8-11]. PL spectra were measured at 300 K at the excitation by a He-Cd laser with a wavelength of 325 nm and a beam power of 50 mW using a PL setup on a base of spectrometer SPEX500. Raman scattering spectra were measured at 300K using a Raman spectrometer of model Lab-Raman HR800 Horiba Jovin-Yvon and a solid state laser with a light wavelength of 532 nm and a power of 20 mW in backscattering configuration.

3 EXPERIMENTAL RESULTS

Figures 1, 2 present the typical PL spectra for nonconjugated (605N, 655N) and bioconjugated (605P 655P) CdSe/ZnS QDs. In nonconjugated state PL spectra of QDs (605N, 655N) are characterized by one PL band with

the symmetric Gaussian shape and the maxima at 2.05 eV (Fig.1, curves 1,2) and 1.89 eV (Fig.2, curves 1,2), respectively, related to the exciton recombination in CdSe cores. At the bioconjugation of QDs with emission of 2.05 eV (605P) the PL spectra have changed a little: PL band peak shifts into high energy on 0.01eV and a half width increases from 120 meV in nonconjugated QDs up to 140 meV in bioconjugated QDs (Fig.1, curves 3,4).

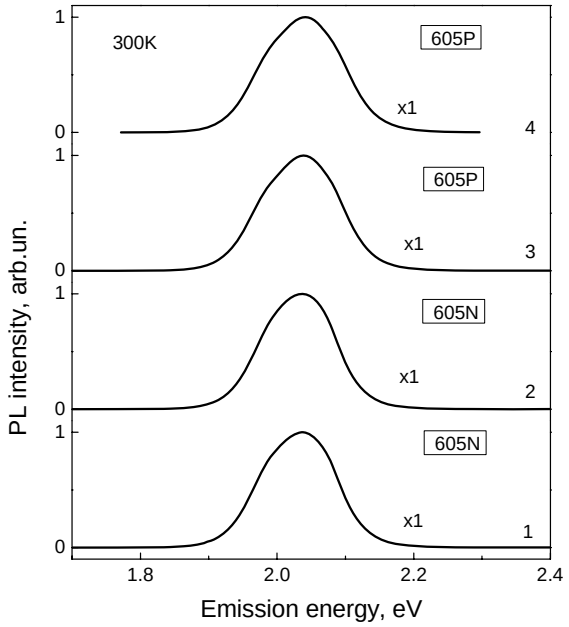

Figure 1: Normalized PL spectra of non-conjugated 605N and bioconjugated 605P QDs measured at 300 K. Numbers at the curves (x 1, x 1, …) indicate the multiplication coefficient used at the normalization of experimental PL spectra.

At the bioconjugation of QDs with emission of 1.89 eV (655P) the PL spectra have changed essentially (Fig.2, curves 3,4). The PL intensity decreases and a PL peak position shifts (48meV) to higher energy from 1.890 eV in nonconjugated QDs up to 1.938 eV in bioconjugated QDs. At the same time the shape of PL bands become asymmetric with an essential high energy tails (Fig.2, curves 3,4).

4 DISCUSSION

A set of possible explanations of PL spectral shift at the QD bioconjugation to antibodies can be related to varying the QD energy levels due to: i) the Stark effect [2, 12] or ii) a compressive strain applied to bioconjugated QDs [2,13].

4.1 QD emission analysis

Actually the first reason can be accompanied by some chemical changes at the surface of QDs connected with the variation of pH value at the QD surface in the bioconjugation process [14]. To distinguish the different reasons it is essential to note that the compressive strain has not change the symmetry of PL bands. Moreover, as Raman scattering study testifies (not shown) the position of Raman peaks related to the LO phonons of CdSe core has not changed at the bioconjugation. These facts, as well as the asymmetric shape of PL band appeared in bioconjugated QDs (Fig.2, curves 3,4), testify that the Stark effect is essential.

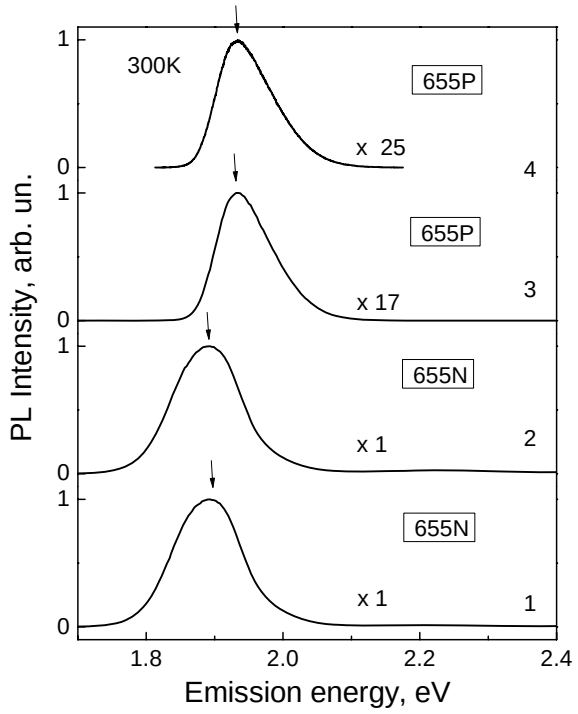

Figure 2: Normalized PL spectra of non-conjugated 655N and bioconjugated 655P QDs measured at 300 K. Numbers at the curves (x 1, x 1, x 17 and x 25) indicate the multiplication coefficient used at the normalization of experimental PL spectra.

It is known that the shift of QD energy levels, ΔE, at the first order Stark effect is directly proportional to the electric field, E_{el}, and to an electric dipole moment, μ_{QD}, of QDs [12]. The QD energy level shift, ΔE, at the second order Stark effect is proportional to the second degree of electric field, E_{el}, and to the polarizability, α_{QD}, of QDs [12]. Both parameters, the electric dipole moment of QDs, μQD, and the polarizability, α_{QD}, increase with enlargement of the QD sizes. The last fact is the reason why the energy shift, ΔE, at the Stark effect is higher for 655 nm QDs in comparison with one in 605nm QDs (Fig.1, 2).

Note in the present model we suppose that an electric field applied to bioconjugated QDs is created by the electric dipoles of antibodies. To confirm the above mentioned model it is important to show that anti IL-10 antibodies

have electric dipole moments. For this aim the Raman scattering spectra have been studied.

4.2 Raman scattering study

Raman spectra of non-conjugated QDs show a high intensity peak at 520 cm-1, corresponding to the optical phonon Raman line from the Si substrate (Fig.3). The intensity of this peak in the Raman spectrum of noncojugated (605N) sample is smaller in comparison with its intensity in bioconjugated (605P) QD samples (Fig.3).

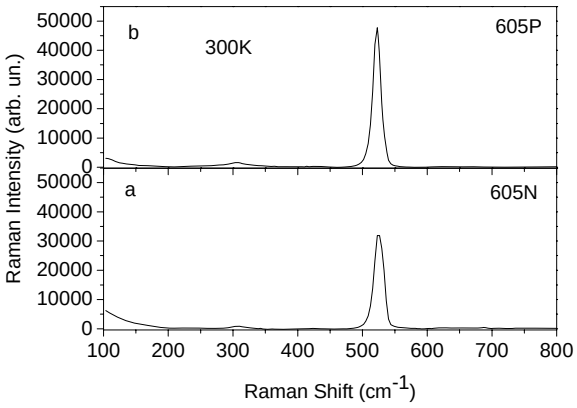

Figure 3: High intensity Raman peaks in Raman spectra of nonconjugated 605N (a) and bioconjugated 605P (b) CdSe/ZnS QDs.

Additionally a set of low intensity peaks at: 211.9, 306.8, 424.3, 619.8 and 667.9 cm-1 has been detected (Fig.4).

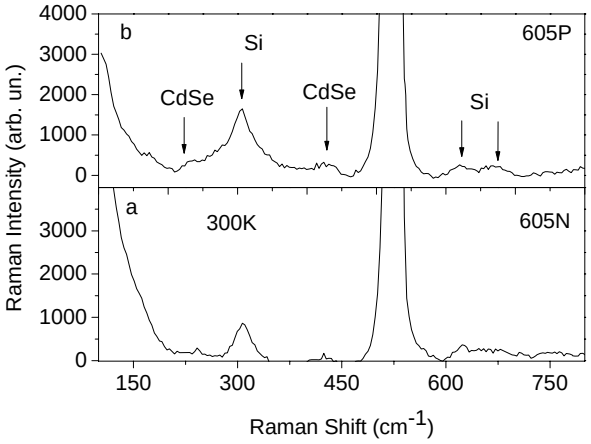

Figure 4: Low intensity Raman peaks in Raman spectra of nonconjugated 605N (a) and bioconjugated 605P (b) CdSe/ZnS QDs.

The Raman peak at 211.9 cm-1 (and its two LO phonon overtone at 424.3 cm-1) corresponds to the LO phonon in CdSe core of QDs. The small shift of LO phonon Raman line (211.9 cm-1) from its position in the bulk CdSe (213 cm-1) has to do, apparently, with the phonon confinement effect in small size QDs (~5.4 nm) [14-16]. Raman scattering in the region of 0-700 cm-1 related to the Si substrate as well. The peak 306.8 cm-1 can be considered as two TA phonon overtones at Raman scattering at the X point of the silicon Brillioun zone [15, 17, 18]. The Raman peaks at 619.8 and 667.9 cm-1 in silicon were assigned to the two phonon peaks, which, as assumed, are the combinations of acoustic and optic phonons in the X and Σ directions of Brillioun zone [15, 17, 18]. In the Raman spectrum of bioconjugated QDs the intensity of all Raman peaks increases essentially and they have seen clearly (Fig.4).

The stimulation of optical field near the surface of illuminated bioconjugated QDs located on the Si substrate and the appearance, as a result, of low intensity Raman peaks at 211.9, 306.8, 424.3, 619.8 and 667.9 cm-1 can be attributed to the surface enhanced Raman scattering (SERS) effect [15,19,20]. As we have shown earlier [8], in general phonons, plasmons or excitons can satisfy to resonance conditions for the enhancement of local electric field. The enhancement of Raman scattering is observed in CdSe/ZnS QDs bioconjugated with anti Interleukin 10 antibodies. This fact testifies that the antibody biomolecules are characterized, actually, by the electric dipole moment that permits them to interact with an electric field of excitation light at the SERS effect. Additionally, the electric dipole moments of IL-10 antibodies create the electric field, Eel, which stimulates the shift of QD energy levels owing the Stark effect in bioconjugated QDs as well.

5 ACKNOWLEDGEMENT

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