THE INFLUENCE OF BIOMOLECULES ON THE LUMINESCENCE OF DEFECTS IN CdSe/ZnS QUANTUM DOTS

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The influence of bio-conjugation on photoluminescence (PL) spectra of CdSe/ZnS quantum dots (QDs), including the luminescence related to defects in quantum dots or at their surface is investigated. It is shown that the luminescence spectra of defects contain two bands. One of them can be ascribed to the recombination of electrons from the energy level of a quantum dot to the level of a Cd vacancy. Another one can be connected with the carrier recombination through donor-acceptor pairs. It is found that the bioconjugation results not only in a high-energy shift of the luminescence band caused by the exciton recombination in quantum dots but also in an increase of the contribution of the defect emission to luminescence spectra. It is shown that the contribution of different defects increases in different ways. The changes in defect emission spectra are explained by an increase of the number of corresponding luminescence centers.

1. Introduction

Colloidal semiconductor quantum dots have attracted considerable interest recently due to their unusual physical properties and wide opportunities of practical applications in optoelectronics, analytical chemistry, biology, medicine, etc. Specifically, this interest is caused by the progress in their fabrication technique which is characterized by a high degree of reproducibility and control [1,2]. The emission spectra of such QDs can be varied easily from blue to red by increasing the size of nanoparticles by several nanometers. However, because of the large surface/volume ratio, the surface defect states, which act as centers of nonradiative or radiative recombination, can influence noticeably the luminescent properties of QDs. Passivation of these defects by organic or inorganic compounds improves essentially the luminescent properties of QDs. In particular, CdSe QDs in a ZnS shell have a luminescence quantum yield of up to 50 % [2]. Nevertheless, in this case, QDs can also remain sensitive to surface defects.

The development of methods of QD binding with biomolecules (bioconjugation) became the basis for making biocomplexes with QDs [3]. This stimulates the use of QDs as luminescent markers in biology, as well as in the diagnostics of different diseases in medicine. However, the influence of the bioconjugation on the luminescent properties of QDs has been studied insufficiently.

Recent investigations of CdSe/ZnS QDs conjugated with various antibodies [4,5] have shown that the bioconjugation results in a spectral shift of the order of several nanometers of the QD luminescence band, which can be used for the visualization of the effect of bioconjugation. In particular, it was found [5] that, drying the samples with a drop of a solution of CdSe/ZnS QDs conjugated with IL10 ovarian cancer antibody deposited on the monocrystal silicon substrate resulted in the ∼15-nm shift of the luminescence maximum of QDs into a short-wavelength length spectral region ("blue" shift). This shift was shown to increase significantly after the annealing of the samples at temperatures of 100–250 °C, and possible reasons for this effect were suggested.

Nevertheless, the influence of the bioconjugation on QD surface states (defects) was not investigated. At the same time, such an influence is expected to occur. In the present paper, the influence of the bioconjugation of QDs with IL10 antibody on the QD and defect-related luminescence bands was studied.

2. Samples and Experimental Technique

Commercial CdSe QDs in a ZnS shell covered with a polymer were obtained from the company Invitrogen Inc. [6]. The average size of these QDs was 2.9 nm. Bioconjugation was performed on a polymeric shell using the method and the conjugation kit proposed by Invitrogen Inc. [6]. Experimental samples were the spots of approximately 3 mm in diameter of a solution of QDs conjugated and non-conjugated with IL10 antibody deposited on a crystalline silicon wafer. Before the initial investigations, the spots were dried in the atmospheric ambience.

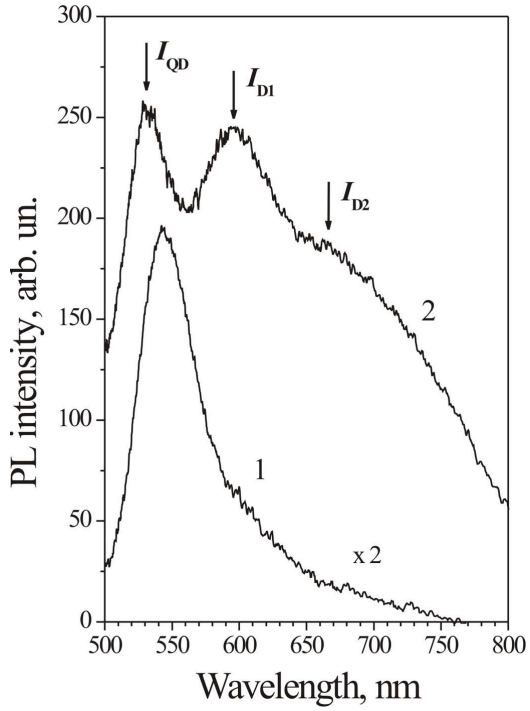

Fig. 1. Photoluminescence spectra of a non-conjugated sample under excitation by a line $\lambda_{exc} = 400$ nm of a halogen lamp. Curve *1* – $T = 300$ K, curve *2* – $T = 77$ K (the values of intensity on a curve *1* are multiplied by 2)

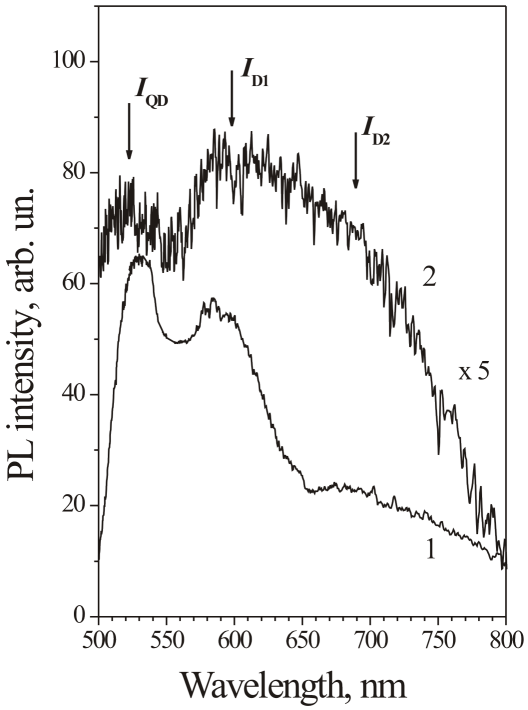

Fig. 2. Photoluminescence spectra of non-conjugated (curve *1*) and conjugated (curve *2*) samples at $T = 77$ K under excitation by a line $\lambda_{exc} = 400$ nm of a halogen lamp

The photoluminescence was excited by light of a halogen lamp passed through a grating monochromator MDR-23 and registered by using a monochromator IKS-12 and a photomultiplier FEU-62.

3. Results and Discussion

The PL spectra of non-conjugated samples measured at various temperatures under excitation at $\lambda_{exc} = 400$ nm of a halogen lamp are presented in Fig. 1. In the spectrum measured at room temperature (curve *1*), the band with a maximum at 545 nm caused by the recombination of excitons in quantum dots (I_{QD}) dominates. This band has also a long-wavelength tail or a shoulder in the region of 600–800 nm. The emission in this spectral region is usually ascribed to the presence of deep levels caused by defects located in QDs or on their surface [7]. The ratio of intensities of these two bands varies from sample to sample.

When the temperature decreases down to 77 K, the intensity I_{QD} increases, and the maximum shifts into the short-wavelength spectral region according to a change of the CdSe band-gap energy (Fig. 1, curve *2*). The defect-related luminescence intensity increases also, but stronger than I_{QD}. Hence, the contribution of the defect emission to the PL spectrum rises. Simultaneously, the defect-related band changes its shape and becomes transformed into a well-resolved peak at 590 nm and a long-wavelength shoulder (Fig. 1, curve *2*). This testifies to the presence of at least two bands corresponding to two radiative centers (D1 and D2) in the defect emission spectrum. It should be noted that the intensity of the long-wavelength component in the defect emission spectrum increases mainly when the temperature decreases.

In Fig. 2, the PL spectra of conjugated and non-conjugated samples measured at 77 K are shown. It is seen that, in the samples with antibodies, the I_{QD} band shifts into the short-wavelength spectral region, and the intensity of luminescence decreases in comparison with that of non-conjugated samples. Simultaneously, the relative contribution of defect-related bands to the PL spectrum increases, and just a contribution of its long-wavelength component rises mainly.

The results listed above show that, despite the presence of the wide band-gap ZnS shell, at least two

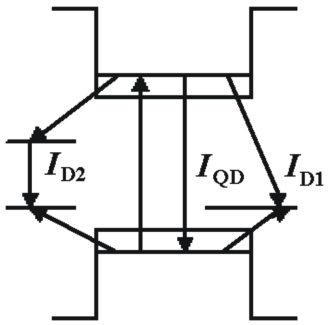

Fig. 3. Schematic illustration of the postulated recombination routes of carriers excited in quantum dots

types of defects that are the centers of radiative recombination and are responsible for two luminescence bands in the spectral region of 600–800 nm exist in quantum dots or on their surface. The short-wavelength defect-related band is located by 0.23–0.35 eV apart from the I_{QD} peak, which corresponds to the energy difference between the Cd vacancy level and the valence band edge in a bulk material [8]. Therefore, it is possible to assume that the long-wavelength defect-related band is caused by the capture of electron from the lowest electron level of QD on a level of Cd vacancy. Such a band was also observed in the case of CdSe and CdSSe QDs in glass [9].

A decrease of the PL intensity occurred when the temperature increases from 77 to 300 K is an evidence of the PL thermal quenching. It is essential that the long-wavelength defect-related band is quenched stronger than the short-wavelength length one. The predominant quenching of the long-wavelength band allows supposing that the centers of radiative recombination related to this band have more than one energy level. In fact, in the case where both emission bands are caused by the radiative capture of a carrier from the same quantized QD level on the corresponding defect levels, the temperature quenching of the long-wavelength band should be weaker than that of the short-wavelength one (i.e., it should occur at higher temperatures) due to a larger energy necessary for the thermalization of carriers of the other sign. Therefore, it has to be assumed that the centers which cause the long-wavelength band have at least two levels, one of which is shallower than the levels of defects which cause the short-wavelength band. These centers can be, for example, donor-acceptor pairs. In Fig. 3, the schematic illustration of the postulated recombination routes of carriers excited in QDs is presented. It should be noted that an idea of that defects which are the centers of radiative recombination in colloidal QDs have a system of levels was expressed in a number of papers [10, 11].

Our results show that, in conjugated samples in addition to the shift of I_{QD} into the short-wavelength region, the whole PL intensity decreases, and the intensity of I_{QD} decreases mainly. The PL intensity reduction can be due to the generation of centers of nonradiative recombination that is caused by the conjugation of QDs with biomolecules. However, in this case, the intensity of all emission bands should decrease by the same number of times. The appearance of traps for carriers generated in QDs can also lead to a decrease of the luminescence intensity. In this case, the capture of one of the carriers by traps can give rise to the Auger process, which results in a reduction of the band intensity I_{QD} [12]. But, in this case, the intensities of all emission bands should also drop in the same number of times, as they have the common excitation channel caused by the light absorption in QDs.

A weaker reduction of the intensity of defect-related bands in comparison with that of the intensity of the band originated from the exciton recombination in QDs is an evidence of some more changes in the system of defects. Specifically, this can be an increase of the concentration of defects which are the centers of radiative recombination. In its turn, the increase of the concentration of radiative centers which cause defect bands can result, by itself, in a reduction of the QD emission intensity. The other reason can be the formation of charged centers on the QD surface. It is known that a charge on the QD surface can reduce the QD exciton emission intensity due to a decrease of the matrix element of electron-hole transitions [13]. Thus, the intensity of defect-related bands can increase, since the excitonic emission in QDs is the competing recombination channel. Apparently, both these causes can explain changes of the intensities of the exciton and defect-related PL bands by different numbers of times, which is observed in the samples after the conjugation with biomolecules.

It is important that the bioconjugation results in an increase of the contribution mainly of the long-wavelength band in the defect emission (Fig. 2). This means that the contributions of different defect-related bands in the PL spectrum change in different ways, which can hardly be explained by the formation of charged centers on the QD surface. Therefore, we suggest that, due to the bioconjugation, there arise the centers of radiative recombination and predominantly the ones which cause the long-wavelength band. In addition, since a decrease of the intensity of all PL bands is observed

in conjugated samples, it should be assumed that the centers of nonradiative recombination or traps, which results in the Auger process, arise together with the generation of centers of radiative recombination. One of the possible reasons for the appearance of recombination centers in conjugated samples can be a decrease, as a result of the bioconjugation, of a degree of passivation of surface defects not detectable in the passivated state. It is also possible that there is the formation of new donor-acceptor complexes.

4. Conclusion

The influence of the bioconjugation on the excitonic and defect luminescences of CdSe/ZnS quantum dots has been investigated. In the defect photoluminescence spectra, two bands are observed. The short-wavelength one is assigned to transitions from the lowest electronic level of a QD on a level of the acceptor, a Cd vacancy, since the maximum of this band is located by 0.23–0.25 eV apart from the maximum of the QD-related band. When the temperature increases from 77 to 300 K, the thermal quenching of the defect luminescence and predominantly its long-wavelength band occurs. This is the evidence of that the corresponding center of radiative recombination has more than one energy level and probably is a donor-acceptor pair.

The bioconjugation results in a short-wavelength shift of the QD luminescence band maximum, a decrease of the luminescent intensity, and an increase of the contribution of defect-related bands (mainly the long-wavelength band) to the PL spectra. The rise of the contribution of defect-related bands to the PL spectra is explained by an increase of the concentration of the corresponding centers of radiative recombination (mainly of those which are responsible for the long-wavelength band). The decrease of the whole PL intensity is caused apparently by the formation of centers of nonradiative recombination.

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ВПЛИВ БІОМОЛЕКУЛ НА ЛЮМІНЕСЦЕНЦІЮ ДЕФЕКТІВ В КВАНТОВИХ ТОЧКАХ CdSe/ZnS

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Р е з ю м е

Досліджено вплив приєднання біомолекул на спектри фотолюмінесценції квантових точок CdSe/ZnS, зокрема, на смуги, пов'язані з дефектами у квантових точках або на їх поверхні. Показано, що спектр випромінювання дефектів складається з двох смуг, одну з яких можна приписати рекомбінації електронів з рівня квантової точки на рівень вакансії Cd, а іншу – рекомбінації носіїв через донорно-акцепторні пари. Встановлено, що приєднання до квантових точок біомолекул приводить не лише до зсуву смуги, зумовленої рекомбінацією екситонів в квантових точках, в короткохвильову область спектра, але й до збільшення внеску випромінювання дефектів у спектр люмінесценції. Показано, що внесок різних дефектів зростає по-різному. Зміни в спектрі випромінювання дефектів пояснюються збільшенням концентрації відповідних центрів випромінювальної рекомбінації.