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Effect of the Polymer on the Photoluminescent Spectrum and Kinetics of Quantum Dots of Cadmium Selenide in Amorphous and Liquid Crystalline Polymer Matrices

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Abstract—Measurements of the photoluminescent spectra and kinetics, and of the excitation spectra of photoluminescence of CdSe nanoparticles embedded in various polymer matrices, show that using a liquid crystalline polymer as a matrix makes it possible to increase the lifetime of photoluminescence and the quantum yield of this process.

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INTRODUCTION

Semiconductor quantum dots (QDs) (nanoparticles in which the movement of charge carriers is limited to three dimensions, altering their energy spectrum) have in recent decades become the subject of intense research. QDs enable us to create materials with new properties, due to the effect of size quantization, highly developed surfaces, and the ease with which they are formed [1–3]. We can in particular control absorption and emission spectra [4], along with the efficiency of nonlinear optical processes in QD ensembles [5, 6], by changing the size and shape of nanoparticles. Of great importance for the optical properties of QDs is that excitons exist inside them at room temperature.

The idea of using QDs as the basis for creating environments where light amplification (and thus lasing) is theoretically possible would seem to be very interesting. If a diameter of QDs is sufficiently small, the quantum limitation of charge carriers alters the forbidden bandwidth and produces an exciton that is stable at room temperature and has an energy structure similar to an atom. This opens up new opportunities for lasing in which the lasing threshold is low and does not depend on temperature. Transitions in a two-level system in semiconductor QDs can be used for optical amplification.

Such semiconductor optical amplifiers operating in the infrared range are normally made on the basis of $A^{III}B^{V}$ compounds [6]. At the same time, the formation of QDs based on semiconductors of the $A^{II}B^{VI}$ group that emit in the visible range is most developed. Indeed, stimulated emission has been detected in tightly packed QDs of CdSe. The introduction of such a condensed fluid into a microcavity results in lasing [7–9]. From a practical point of view, it would be useful to create a nanocomposite medium (e.g., semiconductor QDs in a polymer matrix) in which light amplification is theoretically possible. Polymers are usually transparent in a wide range of the spectrum and are a fairly flexible platform for different optical devices. Such a nanocomposite would have special optical properties that differ from those of the QDs of actual matrices [10, 11]. A number of studies have focused on composites in which the polymer is an inert medium [4] and only immobilizes QDs. Such nanocomposites are of interest for creating waveguides, but lasing has yet to be done in them.

The main factor limiting excitation inside QDs is Auger recombination [6, 12]; a sufficiently high concentration of QDs is therefore a critical condition for light amplification. So-called functional nanocomposites based on QDs in polymers can in this case be quite promising [13]. Ordered QD arrays can form inside them due to self-organized matrices, and the mobility of the QDs is reduced. Low molecular weight liquid crystals and liquid crystalline polymers (LCPs) are among such matrices. Along with anisotropy, which causes certain photonic properties, characteristic features of such matrices are the high sensitivity of liquid crystals and LCPs to the effects of electric, magnetic, and mechanical fields [14–17]. In contrast to nematic and cholesteric LCPs, smectic LCPs can ensure kinetic stability and a homogeneous distribution of QDs. The main features of such systems are the anisotropy of the nanocomposite and the formation of ionic bonds between the matrix and the surfaces of the QDs. As a consequence, nanocomposites containing smectic polymers allow us to attain conditions with high concentrations (over 30 wt %) of QDs without phase separation [18].

The first stage in studying QD nanocomposites in a LCP matrix is measuring their kinetics and photoluminescence (PL) spectra, depending on the concentration of QDs and the type of polymer matrix (LCP or amorphous polymer). The results from such a study are presented in this work.

EXPERIMENTAL

Samples and Measuring Procedures

We studied the dried sol of our initial CdSe QDs, smectic nanocomposites based on 4-(ω-acryloyloxyhexyloxy) benzoic acid that had aliphatic chains with $n = 6$ (BK-6PA) at different mass fractions of CdSe QDs (3, 5, 10, 15, and 30%), along with a nanocomposite based on an amorphous polymer similar in structure and based on 3-(ω-acryloyloxyhexyloxy) benzoic acid PMBK-6A with mass fractions of CdSe QDs of 3 and 15%. The diameter of the QDs was 4.1 nm.

CdSe QDs and polymer matrices were synthesized according to the procedure described in [19]. Nanocomposites based on LCP and amorphous polymers were prepared by introducing a CdSe QD sol into a polymer solution in tetrohydrofuran with constant mixing. The composite solution obtained in this way was precipitated and washed with hexane, and then dried in vacuum to constant weight.

Films of the composites were made as follows. A sample was placed between two polytetrafluoroethylene substrates or two glass slides and briefly heated to a temperature exceeding that of isotropization by several degrees. Films formed as soon as the viscosity of the sample was sufficiently low. The sample between the substrates was then rapidly cooled to room temperature. The films were usually 50–150 μm thick.

The photoluminescence spectrum was studied by exciting the samples with radiation from a pulsed laser based on a Nd:YAG Ekspla 2143A crystal (wavelength, 532 nm; pulse repetition rate, 10 Hz; pulse duration, 25 ps; pulse energy density on the sample, no more than 3 mJ cm^{-2}). Photoluminescence (PL) spectra were recorded with a Princeton Instrument Acton 2500i spectrometer that had a CCD array with a gated amplifier for recording time-resolved PL spectra. Each PL signal was accumulated in 100 ns and averaged over 250 spectra. The PL spectra and the PL excitation spectra were also recorded using a Perkin Elmer LS 55 fluorescence spectrometer.

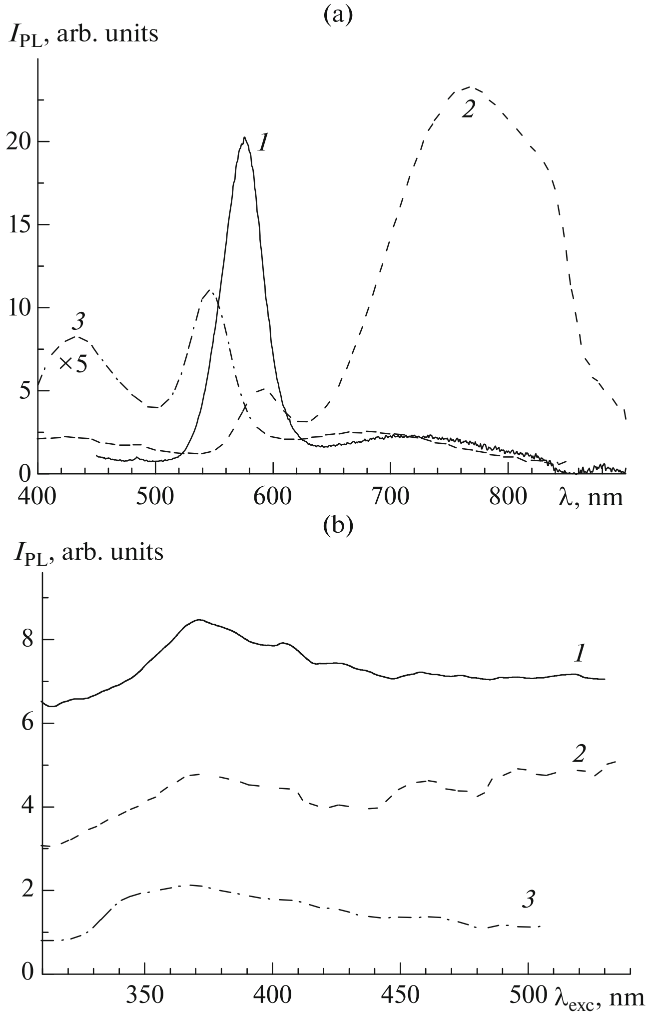

Fig. 1. (a) PL spectra of (*1*) CdSe QDs and nanocomposites with a CdSe QD mass fraction of 15% in (*2*) LCP and (*3*) amorphous polymer matrices when excited by radiation with a wavelength of 368 nm. (b) PL excitation spectra of (*1*) CdSe QDs and nanocomposites with a CdSe QD mass fraction of 15% in (*2*) LCP and (*3*) amorphous polymer matrices, recorded at wavelengths of 576, 595, and 545 nm, respectively.

Photoluminescence Spectra

The PL spectra for the sol of CdSe QDs and for nanocomposites of CdSe QDs in LCPs and amorphous polymer matrices are shown in Fig. 1a. As can be seen, there are two clearly pronounced bands with maxima at wavelengths of 576 and 730 nm (2.15 and 1.70 eV) for the sol of CdSe QDs. The PL spectrum for QDs in a LCP matrix is shifted toward lower photon energies, while the spectrum for QDs in an amorphous polymer matrix is shifted toward higher energies. These PL bands were not detected at QD concentrations below 1 wt %. The short-wavelength band was due to the radiative recombination of excitons in the QDs. The origin of the long-wavelength PL band is

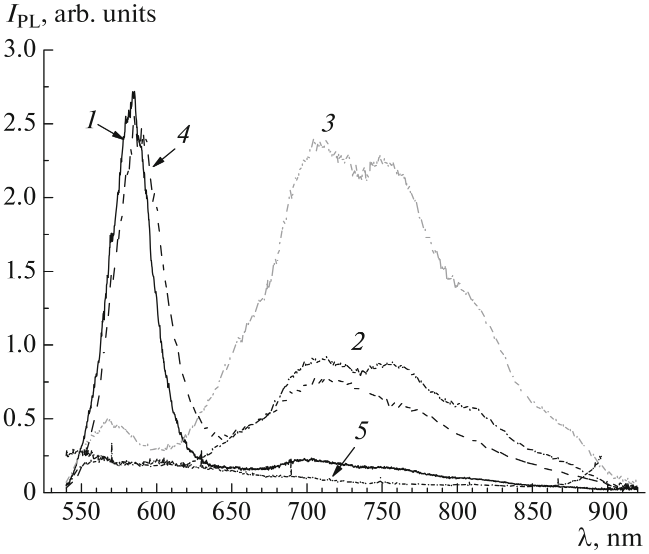

Fig. 2. PL spectra of (*1*) CdSe QD sol; of CdSe QDs in LCP matrices with concentrations of (*2*) 5, (*3*) 10, and (*4*) 30 wt %; and of (*5*) LC polymer when excited by laser pulses with a wavelength of 532 nm.

associated with the levels of surface defects (Se vacancies and states caused by the interaction between QDs and the matrix [19, 20]). This is confirmed by the increase in the contribution from the long-wavelength band to the PL for QDs in the LCP matrix. The sharp drop in PL intensity for QDs in an amorphous polymer, compared to a nanocomposite containing an LC polymer, is noteworthy.

The PL excitation spectra for all three samples are of a similar nature (Fig. 1b). The strongest excitation is observed for the wavelength of $\lambda_{exc} \approx 370$ nm. A drop in PL intensity upon an increase in the excitation wavelength in QD sol and in QDs embedded in an amorphous polymer is observed when $\lambda_{exc} > 370$ nm. In contrast, there is no appreciable reduction in PL intensity for QDs in an LC polymer in this spectral region.

If PL is excited by laser pulses with a wavelength of 532 nm, the PL intensity depends linearly on the intensity of excitation up to 3 mJ cm^{-2}. A change in the intensity of the excitation radiation does not alter the form of the PL spectra.

PL spectra depend on the concentration of CdSe QDs (Fig. 2). The exciton PL band was observed at a concentration of QDs above 3 wt %; its intensity grew along with the concentration of QDs. The dependence of the defect band's intensity on the concentration of QDs was non-monotonic: the intensity for a concentration of 10 wt % was much higher than that of the exciton band, while the exciton band at a concentration of 30 wt % was in contrast more intense (compare spectra *3* and *4* in Fig. 2).

Additional information on the recombination of charge carriers can be obtained by measuring the kinetics of the PLs of the investigated nanocomposites (the data are presented in Table 1). The kinetics of the PL spectra after pulse action is shown in Fig. 3a. As can be seen from the figure, the PL signal in the exciton band fell in less time. There was no notable shift of the peak at different times of spectrum removal. The dependences of the intensity for both the exciton band and the band of surface states are approximated well by the sum of two exponents:

$$I_{PL} = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}},$$

Table 1. Fall times of the fast and slow components of the PL signal and the ratio of their amplitudes in QD sol and CdSe QD nanocomposites in LCP and amorphous polymer matrices

Exciton band								
	CdSe 3%	CdSe 5%	CdSe 10%	CdSe 15%	CdSe 30%	Sol	CdSe 3% (amorphous)	CdSe 15% (amorphous)
τ_1, ns		64 ± 12	63 ± 6	41 ± 7	40 ± 2	53 ± 10	70 ± 40	30 ± 10
τ_2, ns			360 ± 100	200 ± 40	140 ± 10	210 ± 190		123 ± 60
A_1/A_2			8.14	3.15	4.65	11		5.7
Band of surface states								
	CdSe 3%	CdSe 5%	CdSe 10%	CdSe 15%	CdSe 30%	Sol	CdSe 3% (amorphous)	CdSe 15% (amorphous)
τ_1, ns	150 ± 20	160 ± 30	155 ± 10	113 ± 14	122 ± 14	93 ± 20	94 ± 25	64 ± 10
τ_2, ns	650 ± 200	610 ± 340	600 ± 40	450 ± 100	434 ± 64	450 ± 260	324 ± 322	240 ± 40
A_1/A_2	2.07	2.15	2.18	1.61	1.79	2.11	3.52	1.80

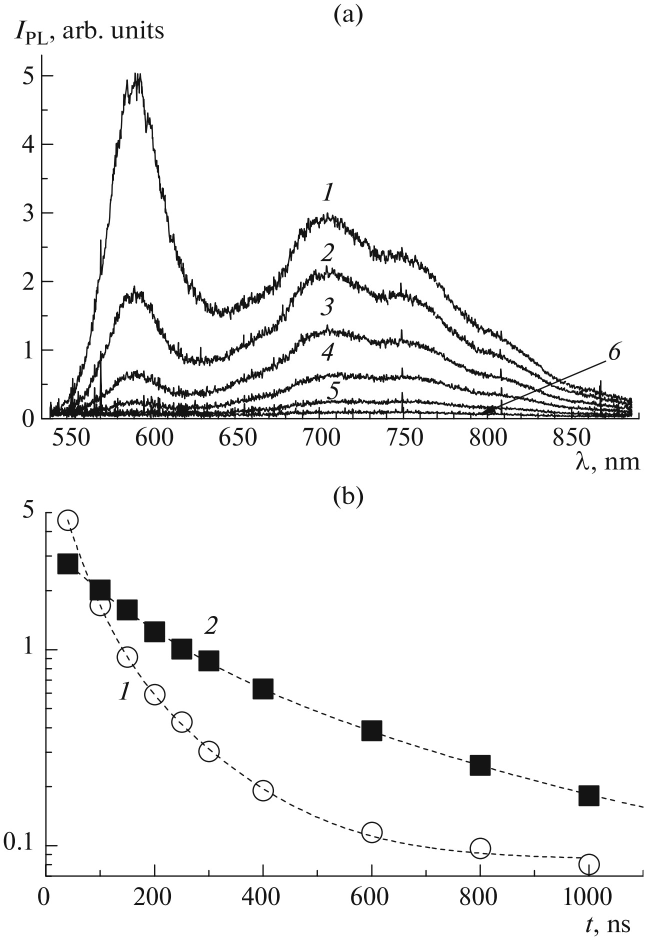

Fig. 3. (a) PL spectra of CdSe QDs in an LC polymer when excited by laser pulses with a wavelength of 532 nm after (*1*) 0, (*2*) 100, (*3*) 200, (*4*) 400, (*5*) 800, and (6) 1500 ns after pulse action; (b) intensity dependence of the PL bands with (*1*) 2.1 and (2) 1.75 eV on time for the sample with a QD content of 30 wt %. The dashed lines show the fitting by the sum of two falling exponentials.

where τ_1, τ_2 are the band lifetimes, and A_1, A_2 are the amplitudes of the exponentials (Fig. 3b).

It can be seen that the lifetime of the exciton band was shortened upon an increase in the QD concentration in samples with an LC polymer. A similar trend was observed in the band of surface states. The use of an amorphous polymer as a matrix shortened the PL lifetime, compared to nanocomposites with an LC polymer. The shortest lifetimes of both bands were characteristic of the amorphous sample with a QD mass fraction of 15%.

Upon raising the concentration of QDs from 10 to 30%, lifetimes were shortened more in the exciton band than in the band of surface states; the relative changes were 50 and around 30%, respectively. A similar trend was observed for samples with an amorphous polymer. Ratio A_1/A_2 of the amplitudes for the fast and slow exponents shrank for the exciton PL band as the concentration grew. This ratio was greatest in the sol. A similar dependence was also seen in the band of surface states, but less clearly. The ratio of the amplitudes was almost halved in the exciton band upon raising the QD concentration from 10 to 30 wt %; such changes did not exceed 20% in the band of surface states. In addition, we can see that the ratio of the amplitudes in the band of surface states was less than in the exciton band.

Amorphous samples exhibited shorter lifetimes than nanocomposites with LC polymers, both in the exciton band and in the band of surface states. Ratio A_1/A_2 in the exciton band for a sample with an amorphous matrix that had a mass fraction of 15% was almost 1.5 times greater than for a sample with an LC polymer with the same concentration. These differences were not as great in the band of surface states, and were around 10%.

Our measurements show that having a matrix increased the number of recombination channels. This shortened the times of the exciton band in nanocomposites, compared to the QD sol. Both the concentration of QDs and the type of matrix affected the lifetime of PL. The lifetimes of PL in nanocomposites with an LCP matrix were double those in amorphous samples with the same concentration of QDs. However, this effect was most pronounced in the exciton band. The band of surface states was less sensitive, both to changes in concentration and to differences in the type of polymer.

CONCLUSIONS

A comparison of the PL spectra and their kinetics for the CdSe QD sol and CdSe QD nanocomposites in the matrix of an amorphous polymer and in the LCP matrix reveals a number of effects of the latter on the charge carrier recombination in these nanocomposites. First, this effect is apparent from the emergence of a high-intensity band of 1.3–2 eV in the nanocomposite with an LC polymer; this band is very weak in the QD sol and in the nanocomposite with an amorphous polymer. Second, QDs with an LC polymer are more efficient and have longer lifetimes than QD nanocomposites with an amorphous polymer with equal mass fractions of QDs in PL nanocomposites. Finally, the efficiency of PL excitation in a QD nanocomposite with an LC polymer does not diminish upon an increase in the excitation wavelength, in contrast to the QD sol and nanocomposite with an amorphous polymer. These features testify to the advantages of using an LC polymer to create nanocomposites with CdSe QDs.

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