Luminescence properties of CdSe nanocrystallites in cadmium alkanoate glasses

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Abstract. Quantum confinement effect and its influence on absorption and photoluminescence spectra of CdSe nanoparticles chemically synthesized in thermotropic ionic liquid crystal of cadmium octanoate are studied. It was found out that the spectral resolution grows with decrease of temperature, so it becomes possible to distinguish the band-edge luminescence from the bands associated with the presence of surface defects. Obtained spectra were analyzed theoretically and the energy diagrams for samples with 1.8 nm and 2.6 nm nanoparticles were calculated.

1. Introduction
Semiconductor nanocrystals (quantum dots, QD) of metal chalcogenides including cadmium selenide attract much attention for half a century, because these media possess vast potential capacity to solve various problems in different fields of activity including material sciences, electronics, biology and medicine. Properties of such compounds, especially their optical properties depend on the size of quantum dots, i.e. on dimensions of the spatial confinement area for electrons, holes and excitons movement [1-3]. Thus the opto-electronic properties of nanocrystals are defined by the quantum confinement effect [4, 5]. Local environment of nanocrystals and methods of their synthesis also influence these properties. Recently more and more complex matrices with anisotropic structure, oriental order and periodicity, such as mesomorphic polymers are used (e.g., [6]) to obtain new materials with appropriate characteristics. One of such new media are liquid crystal matrices of cadmium alkanoates composites with CdSe nanoparticles (NPs), whose absorption spectra and photoluminescence properties were investigated at room temperature in [7]. In the present paper we studied spectral and luminescence characteristics of CdSe quantum dots in cadmium alkanoate glasses in a broad temperature range.
2. Objects of investigation
We have investigated CdSe NPs, chemically synthesized in a thermotropic ionic liquid crystal phase of a cadmium octanoate at high temperature. In the cadmium alkanoate matrices [8], the semiconductor NPs have small size dispersion, they are stable and ordered in a layered smectic A matrix [9]. All cadmium octanoate composites with CdSe NPs were synthesized by T.A. Mirnaya’s group (V.I. Vernadsky Institute of General and Inorganic Chemistry, NAS of Ukraine). The samples of the glassy nanocomposites were prepared by the following method. Polycrystalline powder of synthesized composite was placed between flat substrates and then it was heated to the temperature of liquid crystalline mesophase. After that the sample was cooled rapidly, leading to creation of an anisotropic glass at room temperature [9]. Three types of samples were prepared, containing 1.0 nm, 1.8 nm and 2.6 nm CdSe NPs. Thickness of composite samples was about 10 - 30 μm. The nanoparticles concentration was 4 mol% in all samples.

3. Experiment
Absorption spectra for all samples at room temperature were measured using spectrophotometer Specord M400. Registration of fluorescence spectra and fluorescence excitation spectra was performed by means of the optical system based on the two monochromators MDR-72 with a linear dispersion of 4 nm/mm. The source of excitation light was a 1000W Xe-lamp. Fluorescence spectra were detected on different excitation wavelengths at room temperature, 77 K and 4.2 K.

It should be noticed that quantum yield was increased with the temperature decreasing to 77 K. With further decrease of a temperature to 4.2 K the fluorescence intensity continued to grow, though the spectral peaks positions stood the same compared with ones at 77 K.

![Figure 1](image-url)

**Figure 1.** The absorption spectra (left-hand graph) and fluorescence spectra (right-hand graph) of nanocomposites at room temperature. NPs sizes and corresponding excitation wavelengths are: 1 – 1.0 nm, λexc=393 nm; 2 – 1.8 nm, λexc=387 nm; 3 – 2.6 nm, λexc=387 nm.

4. Results and discussion
In the absorption spectra there are several peaks that can be explained by the presence of NPs with flat form. The double-humped absorption spectra of CdSe NPs are more typical for platelet nanoparticles. In this case the absorption bands at 430 nm and 455 nm can be associated with electron transitions from light hole (LH) and heavy hole (HH) energy levels of valence band to the lowest energy level of conduction band [10]. The absorption spectra clearly demonstrate a size dependent quantum confinement effect. The absorption bands of the CdSe NPs are shifted to the high-energy region relatively to the band gap energy E_g = 1.7 eV of the CdSe bulk crystal [11]. Pure cadmium alkanoate matrices without quantum dots do not absorb light in a visible spectrum.
Both absorption and fluorescence spectra at room temperature consist of separate resonant exciton peaks for a samples with 1.8 nm and 2.6 nm NPs. Decreasing of the NPs size leads to a blue shift in a conjugate spectra. Exciton peaks are the most intensive in the fluorescence spectra (figure 1).

Decreasing of temperature to 77 K causes the following changes in spectra: at 77 K the fluorescence spectrum of the 1.0 nm NPs (figure 2) becomes more structured compared with the room temperature spectrum. There is a short-wave exciton peak with a half-width ~ 15 nm. Between the exciton peak in the fluorescence spectra and the most long-wave band in the fluorescence excitation spectra (that can be related to an exciton transfer) there is a Stokes shift ~ 50 nm. Relative intensity of the long-wave bands at 77 K is much greater compared with the room temperature measurements.

The fluorescence excitation spectra show a blue shift between nanocrystal absorption bands and the band-gap of a bulk CdSe crystal which is about 1.82 eV at 80 K [12]. Further decrease of a temperature down to 4.2 K doesn’t lead to any changes either in peaks position or in half-width values in fluorescence spectra of 1.8 nm and 2.6 nm NPs samples (figure 3).

**Figure 2.** Fluorescence excitation spectra (left-hand graph) and fluorescence spectra (right-hand graph) of nanocomposites at 77 K. Sizes of NPs and corresponding excitation wavelengths are (left): 1 – 1 nm, $\lambda_{\text{reg}}=538$ nm, $\lambda_{\text{exc}}=393$ nm; 2 – 1.8 nm, $\lambda_{\text{reg}}=535$ nm, $\lambda_{\text{exc}}=387$ nm; 3 – 2.6 nm, $\lambda_{\text{reg}}=532$ nm, $\lambda_{\text{exc}}=387$ nm. Fluorescence excitation spectra were recalculated considering the distribution of the radiation source intensity.

**Figure 3.** The fluorescence spectra of 1.8 nm CdSe QD (the same $\lambda_{\text{exc}}=370$ nm) (left-hand graph) and 2.6 nm. CdSe QD (the same $\lambda_{\text{exc}}=430$ nm) (right-hand graph): 1 – at room temperature; 2 – at 77 K; 3 – at 4.2K.
The energy diagrams were built based on the analysis of the obtained spectra for 1.8 nm and 2.6 nm NPs samples in cadmium alkanoate glasses (figure 4). Notes “0” and “1” in the figure indicate energy levels of size-quantization - hole energy level and electron level, respectively; “2” and “3” denote the levels for trapping carriers. \( L \) is absorption energy.

**Figure 4.** Schematic energy diagrams of 1.8 nm CdSe NPs (left-hand graph) and 2.6 nm CdSe NPs (right-hand graph) in cadmium alkanoate glasses. See the text for notations.

Transition 1-0 represents an exciton band in a fluorescence spectrum. Transitions 2-0 and 3-0 are corresponded to the long-wave bands. Rates \( \gamma_0 \) and \( \gamma_0' \) characterize radiative and non-radiative recombination of electrons and holes in the size-quantization levels, respectively. Besides the band-edge transition there are two processes of trapping non-equilibrium carriers from the size-quantization levels to the shallow traps: 1-2 and 1-3 with corresponding rates \( \gamma_1'' \) and \( \gamma_2'' \) for electrons.

Assuming \( n, n_1, \) and \( n_2 \) as the average number of the electron-hole pairs in the appropriate states per one NP, the balance equations for 1.8 nm CdSe NPs will be following:

\[
\dot{n} = L - (\gamma_0 + \gamma_0' + \gamma_2') n, \\
\dot{n}_1 = \gamma_1' n - (\gamma_1 + \gamma_{10}) n_1, \\
\dot{n}_2 = \gamma_2' n - (\gamma_2 + \gamma_{20}) n_2. 
\]

Solving equations (1) for the case when \( \dot{n}_1 = 0 \), the spectral bands intensities can be found as:

\[
I = \gamma_0 n, \quad I_1 = \gamma_1 n, \quad I_2 = \gamma_2 n.
\]

One can obtain from the equations (1) that the excitation intensity \( L \) doesn’t influence the relative fluorescence intensities (\( I / I_1 + I_2 + I_3 \) etc). Other parameters are expressed in the units of \( \gamma_0 \) of the main transition. Radiative rates \( \gamma_0 = \gamma_1 = \gamma_2 = 1 \). Non-radiative rates were used in the following form: \( \text{Const} \cdot e^{-0.05/kT} \) in accordance with the work [13], where 5 nm CdSe QDs were studied. Values of the rates had been selected so as the measured spectrum was in close agreement with one calculated using the equations (1). Probability of \( \gamma_2'' \) transition is many orders smaller than the others, so it wasn’t considered in calculations. All spectra were approximated by Gaussian functions.

**Table 1.** Values of the non-radiative constants for fluorescence spectra of 1.8 nm and 2.6 nm NPs.

| QD size (nm) | \( \lambda_{\text{exc}} \) (nm) | \( \gamma_0' \) (× \( e^{-0.05/kT} \)) | \( \gamma_1' \) | \( \gamma_2' \) | \( \gamma_1'' \) (× \( e^{-0.05/kT} \)) | \( \gamma_{10} \) (× \( e^{-0.05/kT} \)) | \( \gamma_{20} \) (× \( e^{-0.05/kT} \)) |
|--------------|----------------------|-----------------|-----|-----|-----------------|-----------------|-----------------|
| 1.8          | 387                  | 170             | 4.14| 11.52| -               | 2               | 50              |
| 2.6          | 410                  | 26              | 1.50| 2.70| 400             | -               | 50              |
The optimized values of non-radiative constants for fluorescence spectra of the samples containing 1.8 nm and 2.6 nm CdSe NPs are given in the table 1.

Figure 5. Luminescence spectra of 1.8 nm (left) and 2.6 nm (right) QD nanocomposites, measured: 1 – at room temperature and 3 – at 77 K, and calculated using the equations (1): 2 – at room temperature, 4 – at 77 K.

The examples of calculated spectra of 1.8 nm and 2.6 nm CdSe nanocrystals at room temperature and 77 K are shown in the figure 5.

5. Conclusion
We have measured absorption and luminescence spectra of CdSe NPs with average size of 1.0 nm, 1.8 nm and 2.6 nm which are chemically synthesized in thermotropic ionic cadmium octanoate liquid crystal. Anisotropic glassy composites with CdSe NPs are obtained by rapid cooling from mesophase to the room temperature. Obtained spectra were analyzed theoretically and the model of electron levels of CdSe nanoparticles is offered. Developed theoretical approach satisfies experimental data with quite high accuracy to a first approximation. In the future, we are going to perform a more detailed analysis of these spectra and consider their relation with the structure of the CdSe NPs.

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