The study of CdSe colloidal quantum dots synthesized in aqueous and organic media

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Abstract. The samples of CdSe colloidal quantum dots (CQDs) synthesized in aqueous and organic media are studied. The possibility of luminescence peak position control depending on nanoparticle growth process is demonstrated. The samples synthesized in organic medium revealed the luminescence color variation effect with nanoparticle growth. The relation of this effect with processes of nucleation and defect formation in nanoparticles is considered. The CQDs of CdSe coated with CdS shell are fabricated. The use of inorganic shell can provide a double increase of the luminescence quantum yield.

1. Introduction
In the past decade, the studies on colloidal quantum dots (CQDs) have been developed widely. CQDs are semiconductor particles of nanometre-scale synthesized in liquid media and having unique properties. Because of the small geometric dimensions the CQDs reveal quantum size effects. These objects can be considered as "artificial atoms", their properties can be relatively easily controlled by varying the synthesis process parameters. The low cost and easiness of the techniques for synthesis CQDs stipulate broad prospects for their use in new nano- and optoelectronic devices. Colloidal quantum dots can be used for a high-performance LED and laser structures creation, as well as photosensitizers in solar cells or luminophores in micro-devices for biological tissues optical tomography. This article presents a method for the creation of colloidal quantum dots based on cadmium selenide, which allows controlling the wavelength of the radiation due to temperature and synthesis duration regulation.

2. Experiment
In order to study quantum dots properties and characteristics the non-invasive optical spectroscopy techniques were employed. These techniques are based on the use of photoluminescence effects and allow obtaining information regarding particle size, crystal structure quality, quantum yield, monodispersity and other CQDs parameters [1].
A measuring device based on a quick scan spectrometer (QSS) Ocean Optics USB-4000 allowing photoluminescence full range registration in a short time period was adjusted and configured in order to study the photoluminescence spectra. The sample in a quartz cell was placed into special holder and was excited by a focused laser radiation at a wavelength of 445 nm. The photoluminescence signal was collected by the collimating optical system and was directed to the input QSS by means of a fiber. Data from the spectrometer was analyzed automatically by means of specialized software designed in the LabView environment.

Several series of samples were synthesized. Synthesis was carried out in aqueous and organic media with the use of various precursors. CQDs which constitute CdSe cores covered with broad-band CdS were obtain in the same manner. The photoluminescence spectra measuring of fabricated samples was carried out.

The synthesis of colloidal CdSe quantum dots in organic medium was carried out in the first part of the work. Cadmium precursor solution was prepared by mixing CdO, oleic acid and liquid paraffin followed by heating to 150˚C. Selenium precursor was obtained through heating selenium powder and liquid paraffin mixture to 220˚C. The introduction of cadmium containing solution into selenium precursor was carried out at the temperature of 240˚C. Samples were obtained at intervals of 1, 2 and 5 minutes. Figure 1 shows the photoluminescence spectra of the synthesized CQDs.

Figure 1. Normalized PL spectra of CdSe quantum dots as function of time: (a) 1 min, (b) 2 min, (c) 5 min after injection. Organic medium.

The spectra reveal two radiation regions: a high intensity peak on the left side of the characteristics and a broad plateau of a lower intensity on the right. We consider luminescence peak on the left that shifts from 470 nm to 520 nm wavelength with synthesis time to correspond to intraband transition. It is caused by the CQDs size increasing during the CQDs synthesis that leads to a decrease in the effective width of the band gap so that the emission shifts to a long wave region. The peak half-width was approximately 50 nm and decreased slightly in the course of the reaction which can be attributed to improved surface states passivation with oleic acid. The occurrence of plateau in the long wave region of the graph can be explained by existence of the QD surface defects that act as trap levels within band gap and provide the route for concurrent radiative recombination. With time oleic acid
molecules passivate these surface states more efficiently and as a result the photoluminescence intensity caused by defects decreases comparatively to intraband emission.

The synthesis of CdSe colloidal quantum dots in aqueous medium was carried out in the second part of the work. Thioglycolic acid (TGA) was applied as a stabilizer. The synthesis was conducted during a long period with a gradual temperature increase. Samples were taken from the reaction medium in certain time intervals. CQDs were synthesized in almost boiling distilled water in the same manner. The molar ratio of the solution components was \([\text{TGA}] : [\text{Cd}] : [\text{Se}] = 1.4 : 1 : 0.6\). Temperature of the synthesis maintained at 97°C. Figure 2 shows the luminescence spectra of colloidal quantum dots built in relative units.

![Figure 2](image.png)

**Figure 2.** Normalized PL spectra of CdSe quantum dots as function of time: (a) 0.5 min, (b) 6 min, (c) 25 min, (d) 60 min, (e) 90 min after injection. Aqueous medium.

The luminescence peak shifted to long wave region with time. The spectrum half-width decreased from 200 nm for the first sample to 150 nm for the last one. The luminescence peak shift is caused by colloidal quantum dots growth in the course of the reaction. Rapidity of this process noticeably decreases with time. This is probably due to the mechanism of colloidal nanocrystal growth known as Ostwald ripening [2]. Nanoparticles grow not only due to the Cd and Se individual atoms, but also due to the fact that larger quantum dots absorb smaller ones. Over time the number of small-sized quantum dots is greatly reduced because most of them are absorbed by larger crystals. The complete depletion of Cd and Se occurs in the reaction medium. As a result further growth of quantum dots terminates or proceeds very slowly. The reduction of the spectra half-width can also be explained by the absorption of small nanoparticles by larger dots.

The main method to estimate the size of colloidal quantum dots into the liquid medium, is the study of optical absorption spectra [3-6]. Existence of exciton peak in this spectrum indicates that the sample contains CQD’s [4]. Size of colloidal quantum dots can be calculated from exciton peak position [5]. Calculations show that for our sample particle size was 1.5 - 2.5 nm, which makes it difficult to study their structure directly. It is known [6], that the luminescence in the CQD’s can occur in two ways – by interband transitions or by transitions through traps arising due to defects on the surface of the
particles. In the first case, the Stokes shift is relatively small, in the second case, it may exceed 200 nm.

Figures 3 and 4 shows the absorption spectra of the CQD’s synthesized in aqueous and organic media respectively. The spectra are very similar. The first exciton peak is near 450-500 nm. There is a shift of the peak to longer wavelengths, indicating an increase in particle size with increasing time of their synthesis. Comparison between absorption and luminescence spectra for CQD’s synthesized in aqueous media shows that Stokes shift is quite large. The same mechanism of emission causes the appearance of a plateau on the luminescence spectra of the samples synthesized in organic media. Shortwave narrow peaks result from interband transitions. The occurrence of such peaks indicates a lower density of defects in the samples of this type.

![Figure 3. Normalized ABS spectra of CdSe quantum dots as function of time: (a) 0.5 min, (b) 6 min, (c) 25 min, (d) 60 min, (e) 90 min after injection. Aqueous medium.](image)

The next experiment was carried out to coat CdSe CQDs with the broad-band CdS shell. Figure 5 shows the photoluminescence spectra of obtained samples.

Sample 0 represents the initial CdSe colloidal quantum dots obtained in aqueous medium by the same method as in the previous experiment. Sample 1 was prepared as follows. The initial CdSe solution and the Cd-TGA solution were mixed in a flask. Cd-TGA solution contains Cd 2.5 times as much as CdSe. Further, a solution of Na₂S ([Cd]/[S] = 1:1) was added dropwise during 25 min. A slight spectrum shift towards shorter wave regions was observable. The most noticeable result was the increase in photoluminescence intensity that is conditioned by the passivation of the surface states by broad-band CdS. Sample 2 was obtained by introducing the Na₂S ([Cd]: [S] = 10:1) in the initial solution during 2.5 min. Thus, we can conclude that intensity is significantly reduced by the surface states. The broad-band CdS with increased molar cadmium content passivated to the best advantage. A slight luminescence peak shift towards shorter wave region is probably associated with reduction in the crystal structure, and correspondingly influence thereof on the photoluminescence spectrum, and also due to the presence of broad-band CdS.
Figure 4. Normalized ABS spectra of CdSe quantum dots as function of time: (a) 1 min, (b) 2 min, (c) 5 min after injection. Organic medium.

Figure 5. The photoluminescence spectra of CdSe nuclei without shell (0) and coated with shell (1, 2). Aqueous medium.

3. Conclusions.
The colloidal quantum dots of CdSe were created in organic and aqueous media, and further their parameters dependence on the synthesis was studied. The high temperatures of the synthesis were revealed to beneficially affect the quality of the CQD crystal structure. The photoluminescence
emission intensity of the samples synthesized at high temperatures is significantly greater than the photoluminescence intensity of the samples synthesized at low temperatures. With increasing the synthesis time the particle concentration decreases. This should be taken into account when estimating the quantum yield. The broad-band CdS coating results in the surface states passivation and two times increase in intensity of photoluminescence.

The quality of the crystal structure may be estimated by measuring the intensity of photoluminescence. The defects in the crystal structure increase the possibility of non-emitting transitions. Thus, CQDs synthesized in organic media have less defective crystal structure as it allows applying higher temperatures.

We estimated the dispersion of the average size of the particles. Minimum particle size variance is observed in the samples synthesized in the organic medium. This phenomenon is caused by the high temperatures of the synthesis. In aqueous media, the luminescence peak width decreases with an increase in the synthesis time. This is due to the predominance of the growth mechanism called Ostwald ripening in the later stages of the synthesis.

The obtained array of CQDs are intended for use as luminophore [7] in order to create micro-devices for biological tissues optical tomography. Moreover, we carry out a work on the elaboration of white LEDs with high CRI based of nitride-structures and luminophores of colloidal quantum dots [8]. We actively develop tunable lasers in a wide range of wavelength. We design a new type solar cell with a selective absorption with using in their construction varied photodetectors including solar-blind detectors [9].

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