The luminescent structures based on colloidal quantum dots CdZnSeS/ZnS

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Abstract. Phosphor mixture based on colloidal quantum dots (CQDs) has been developed. Devices based on nitride LEDs and phosphor mixtures of CQDs have been created. CRI value of the devices exceeded 95.

1. Introduction
In the last decade optoelectronic devices based on colloidal quantum dots are being actively developed [1]. CQDs are nanoscale particles [2] that are placed in the solution and that retain their state as a result of passivation properties of surfactants. Such nanoscale particles can be prepared by using relatively inexpensive colloidal synthesis techniques. These techniques do not require complex equipment [3-8]. In this case, properties of colloidal quantum dots depend on the initial materials and technological parameters of the synthesis. The most important property of CQDs as quantum-sized particles is the dependence of their energetic parameters from geometric dimensions. This allows to adjust characteristics of CQDs by changing technological parameters of the synthesis [9-11]. One of the promising semiconductor devices are QD-based WLEDs [12] and LEDs coated with phosphor mixtures of the CQDs with the colour rendering index (CRI) close to 100. During this study, we created three prototypes of such devices. We based them on semiconductor light-emitting diodes with wavelengths of 290 nm, 360 nm and 405 nm.

2. Description of investigated CQDs
We used three compositions of CQDs to create light-emitting structures. First composition was based on cadmium sulphide (CdS) CQDs with peak wavelengths of 380, 400, 420, 440, 460 and 480 nm. Second composition was based on CdZnSeS solid solution, covered with wide-band shell of ZnS, with peak wavelengths of 500 and 550 nm. Third composition was based on CdSe, also covered with wide-band shell of ZnS, with peak wavelengths of 600, 650 and 680 nm.

3. Calculation of phosphors. The interaction between CQDs.
Before creating luminescent structures, we studied interaction of colloidal quantum dots mixed in a solution and after deposition on the substrates of different types. Interaction between the CQDs in the mixture, in most cases, led to an increase in the intensity of the longwave part of the spectrum and to a decrease of the intensity in the shortwave part of spectrum. We studied these interactions in detail. Parameters of interactions were determined for the colloidal quantum dots based on cadmium sulphide, cadmium selenide and solid solutions thereof. Obtained interaction parameters were in a form of an array of calibration coefficients, taking into account the effect of the substrate and the method of coating.
Calibration coefficients were entered into further described algorithm and software for calculation of the spectral characteristics of luminescent structures. It is shown that the strongest interaction is manifested for the non-enveloped structures. In some cases, this interaction was so strong, that it almost entirely suppressed their luminescence as a result of agglomeration and radiation. Developed technique prevented agglomeration through the use of polymer matrix, layer deposition of various types of particles arrays and their subsequent annealing.

Quantum dots of different sizes can be used to construct the spectrum of arbitrary form. Spectrum of the solar radiation at the earth's surface is one of the most important spectra for the analysis of the colour characteristics. This spectrum can be simulated using a popular approach, which essentially is an approximation of the solar spectrum to spectrum of the reference blackbody at a given temperature. The simulation showed that the spectrum with a CRI of 99.5 can be obtained from mixtures based on ten samples of CQDs different sizes.

4. Technology of creation of phosphors

We used the following particle deposition methods: drip coating method, spin-coating, spray atomization (microdroplet method) or soaking. Next, a layer of deposited quantum dots was dried or annealed. Most frequently used combination was drip deposition and centrifugation, followed by annealing in vacuum at temperatures of 30 - 150°C for 3 - 30 minutes depending on the concentration and composition of CQDs. To obtain desired density and distribution of colloidal quantum dots on the substrate surface, these procedures were carried out repeatedly.

Selected CQDs samples had their required wavelength of the radiation in the visible range. Spectra outside the visible range were not considered. Two parameters controlled the intensity at the corresponding wavelength: concentration in the initial solution of CQDs and quantum yield of the corresponding sample. The concentration of CdS and CdSe CQDs in the initial solution was 5 mg/ml and 100 mg/ml, respectively. Therefore, CdSe CQDs samples were diluted to appropriate values. The quantum yield for the CdS and CdSe CQDs was 10% and 15-80%, respectively. The resulting mixture was deposited on a glass substrate, including quartz, and annealed for complete evaporation of the solvent. In some cases, the operation was repeated in order to increase the density of the particles to the desired values.

Thus, we were able to develop luminescent emitting devices based on CQDs of metal chalcogenides by choosing the appropriate structure, taking into account calibration coefficients and making appropriate modelling. In this research we used the reference light sources of devices with colour temperatures of 6504 K and 5503 K. The source of characteristics corresponded to solar radiation.
spectrum and took into account the absorption of the earth's atmosphere. Created devices were based on multi-component mixtures of cadmium sulphide and cadmium selenide CQDs, and solid solutions thereof, deposited on the substrate.

| Figure 2. The luminescence spectrum of emitter based on the CQDs with a colour temperature of 6504 K | Figure 3. The luminescence spectrum of emitter based on the CQDs with a colour temperature of 5500 K |
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Luminescent emitting devices with high colour rendering index were created based on the established structures (Figure 4). Devices were a system of LEDs with luminophore placed in a single package. LEDs were used as emitter with different luminescence wavelengths in the ultraviolet and violet region (290, 360, 405 nm). It was best to use an ultraviolet emitter with wavelength of 290 nm because its radiation does not fall into the visible range and does not distort the shape of the spectrum.

| Figure 4. Fluorescent emitter based on the system LED + luminophore |
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We searched for optimal design for the structure, converted the largest part of the pump radiation into visible light, and selected the best thickness of the luminescent layer and concentration of the CQDs. The shape of the spectral characteristics of the emitting devices was fully compatible with the spectra of luminescent structures and depended insignificantly on the current in the LED. We used LEDs with radiation wavelengths of 360 and 405 nm to reduce the cost of devices. The main difference in the spectra for these emitters in the short-end of the range was in an additional component associated with partial penetration through the substrate of the LED radiation.
Figure 5. The emission spectrum of the luminescent device based on LED, with a peak wavelength of 360 nm

Figure 6. The emission spectrum of the luminescent device based on LED, with a peak wavelength of 405 nm

High temperature stability characteristics were achieved through the use of quantum dots in reemitting layers. The possibility of implementing almost any form of spectral characteristics of the luminescence devices is especially important. In many cases, the process is very complicated when using luminophores based on other materials.

As a result, we created the reference light sources devices with colour temperatures of 6504 K and 5503 K. The source of the characteristics was is correspondence with the solar radiation spectrum, and took into account absorption of the Earth's atmosphere. Method of creating such devices with almost any desired shape of the spectral characteristics in the visible spectrum range was developed.

5. Conclusion
Created luminescent structures showed efficiency of using CQDs to create light-emitting structures with spectral characteristics of given shape. We showed that the use of a mixture of three or four types of CQDs allowed to obtain a high colour rendering index.

We estimated the parameters that had influence on interaction CQDs when mixed and deposited on the substrate. We established that the blending CQDs with the shell and without the shell in liquid form leads to aggregation and suppression of luminescence. The solution of this problem was to deposit layers of mixtures of different types of CQDs. During creation of light-emitting structures we deposited first narrow-band and then wide-band samples of quantum dots.

Created light-emitting structure corresponded to the three standards: the spectrum of the sun on the earth's surface, blackbody at 5500 K and blackbody at 6504 K. These structures had a colour rendering index CRI = 95 ... 97.

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