

Optical parameters of ITO/TPD/Alq3/Al luminescent structures, containing arrays of CdSe/ZnS colloidal quantum dots

I I Mikhailov, S A Tarasov, I A Lamkin, P O Tadtaev, L I Kozlovich,
A V Solomonov, E M Stepanov

Saint Petersburg Electrotechnical University «LETI» (ETU)

E-mail: iimihalov@gmail.com

Abstract. The luminescent organic ITO/TPD/Alq3/Al structures and CdSe/ZnS quantum dots (QD) arrays were created. Electrical and optical properties of the samples were examined. The luminescence of the layers and QD arrays was shown in the range of wavelengths from 400 to 680 nm. Luminescent structures with phosphors corresponding to the emission standards with CRI>98 and with color temperature of 5500 K and 6504 K were created.

1. Introduction

For the last decade colloidal quantum dots (CQDs) have become an object of particularly intensive studying [1]. CQDs are semiconductor particles of nanometer scale synthesized in liquid media and characterized by unique properties which substantially differ from bulk material properties. One of the most important advantages of CQDs is a facility of geometric size tuning through technological parameters variation (time, temperature etc.). The procedures of their synthesis do not require expensive equipment and materials. CQDs are a promising material [2] for the creation of high-performance LED and laser structures, as well as photosensitizers in solar cells or phosphors in micro-devices for optical tomography of biological tissues. The application of CQDs in the creation of the organic light emitting structures such as OLEDs is of special interest. Insertion of CQDs into OLED structures provides the substantial increase in luminescence efficiency without seriously complicating the techniques of creating light-emitting structures.

2. Materials and methods

In this article, attention is paid to the study of CdSe/ZnS and CdSeZnS/ZnS colloidal quantum dots with peaks of photoluminescence in the range of wavelength from 500 to 680 nm. Surface shell of quantum dots by wide bandgap shell of ZnS significantly improves their properties. Concentration of the surface defects in such particles is greatly reduced. It leads to noticeable increase in luminescence quantum yield. In addition, the oxidation resistance of shell CQDs increases. Nevertheless, were also investigated nonenveloped CQDs CdS. This provided an opportunity to compare their basic optical parameters. It is



also allowed to extend the range of luminescence of produced arrays of CQDs toward shorter wavelengths to 400 nm.

CQDs deposition techniques on the substrate have been tested. These techniques allow retaining high emission properties without significant loss in the luminescence efficiency for all types of particles. As substrates used were different plates of crystalline and amorphous materials [3], promising for creating organic light emitting diodes (OLED) and other luminescent devices. The large number of samples has been created based on glass and quartz substrates without the use of additional layers. The deposition of CQDs was carried out by centrifugation or by applying microdroplets using for a part of structures subsequent annealing in an inert atmosphere [4].

Essential optical and luminescent properties of CQDs were measured and carefully analyzed [5-7]. Experiments were performed on the installation, based on the double-grating monochromator SDL-1, which enabled the optical resolution of 0.01 nm. Ocean Optics USB-4000 и HR4000 fast scanning luminescence spectrometers were applied also. 445-nm semiconductor laser, 290-nm optical emitter, mercury vapor and other gas lamps were used to excite the emission. The lock-in amplifier Stanford SR-810 was applied in order to increase the sensibility of the installation.

3. Results

Figure 1 shows the luminescence spectra of colloidal quantum dots of various composition and size, deposited on the substrate. CQDs deposited arrays were obtained, luminescence parameters, which almost did not differ from the characteristics of the particles present in the solution. It was shown that photoluminescence of deposited CQDs based on CdSe with shell still was mainly caused by excitonic transitions. It was confirmed by the study of the absorption spectra. It is shown that the first exciton absorption peak is close to the maximum of the luminescence spectrum of such dots. In addition, on the graph is no long-wave radiation, which is characteristic for transitions involving surface states. It indicates the high level of surficial defect passivation due to the application of wide-bandgap ZnS shell.

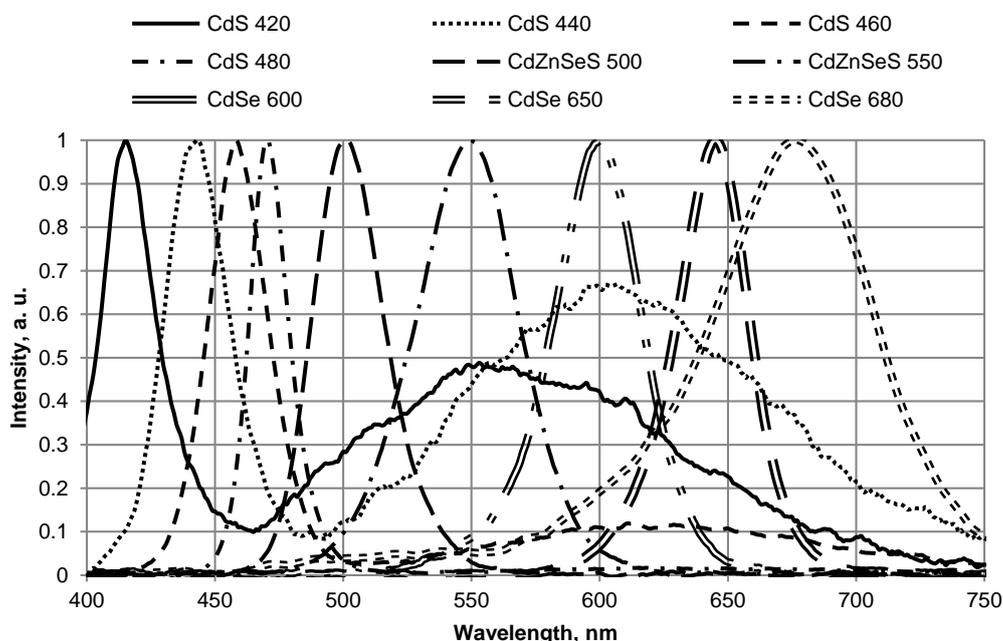


Figure 1. The luminescence spectra of CQD's.

For samples based on non-enveloped CQDs based on CdS is observed the broadened line at wavelengths of 500-750 nm (Figure 1). This is explained by the influence of transitions involving surface states. Radiation in this range is observed in nanoparticles, which are in the colloidal solution.

Although in some cases, the existence of such a wide range of radiation is necessary to recognize drawback investigated material. In the article, this effect is found useful application. Using such CQDs white phosphorus coatings were created based on a small number of components. Color parameters of such coatings are similar to the characteristics of white LEDs based on InGaN. CdSe 500 an additional component has been applied to improve the parameters of these phosphor coatings (Figure 2a). This is allowed to smooth cavity in the green region and achieve CRI > 90.

To further improve the color characteristics and the luminescence efficiency of the phosphor layers properties of combined arrays CQDs containing nanoparticles of various compositions and sizes was simulated. Calculations have shown that it is possible to create phosphors, CRI which is practically equal to 100. To create coatings with high CRI were conducted experiments to study the deposition techniques of CQDs arrays with different composition and their luminescence properties. We were determined coefficients depending on the initial concentration of particles in the solution and on the efficiency of luminescence. It was also determined the effect of particles arrays deposition techniques, substrate and annealing. The processes of interaction of nanoparticles of various types that make up the array are also considered. It is allowed to create phosphor coating, CRI that exceeded > 98. The structures corresponding emission standards with the color temperatures of 6504 K (Figure 2a) and 5500 K (Figure 2b) and solar radiation on the ground have been developed.

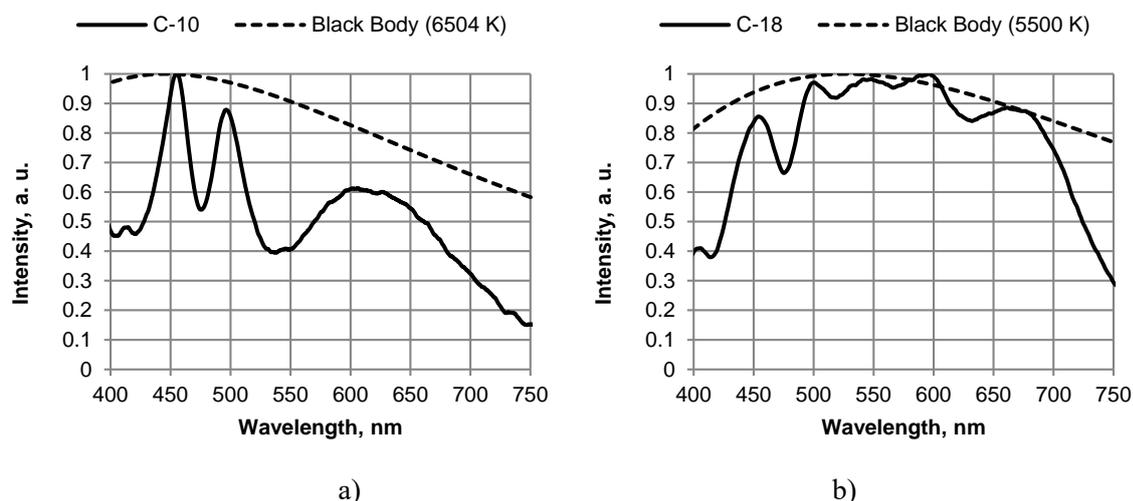


Figure 2. White phosphor coatings based on colloidal quantum dots CdSe (a) and structures with improved CRI (b).

The calculation of the CQDs' dimensions, based on their absorption and photoluminescence spectra, was run and it was shown that the diameter of the core was to range from 3 to 6 nm. The substantial divergence between the SEM data and results of the modelling might be explained by the fact that the calculation didn't take wide-bandgap shell's and surfactant's dimensional parameters into account. Therefore, the thickness of the outer shell might be estimated at 5-7 nm.

Previously examined CQDs were inserted into the active layer of the OLED as the deposited array of nanoparticles. The general OLED structure is a complex system of several thin layers between two electrodes, one of which is transparent to allow the emittance the light. The simplest structure is a single-layer device architecture, where the organic emitter is deposited between anode and cathode. More complex structures have a total of 7-9 active materials: an anode; anode buffer layer (ABL), hole injecting layer (HIL) or electron blocking layer (EBL); hole transporting layer (HTL); emissive layer (EML); electron transporting layer (ETL) or hole blocking layer (HBL), electron injecting layer (EIL); cathode buffer layer (CBL), a cathode and a protective barrier layer. Excitonic radiative transitions provide the growth of luminescence efficiency. Insertion of the CQDs also provides allowance for the OLED spectrum tuning by controlling QDs' sizes, structure and composition.

ITO/TPD/Alq3/Al OLED structures were created (Fig. 3a): TPD (N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine) was a hole transporting layer, Alq3 (Tris(8-hydroxyquinolino)aluminum) was an emissive/electron transporting layer, aluminum and ITO (indium tin oxide) were used to create electrodes. All the layers were deposited by means of spin-coating or vacuum thermal evaporation on the glass substrate. The process of deposition lasted no more than several seconds which positively affected the quality of the layers. The upper contact was created of the magnesium or aluminum by vacuum resistive coating.

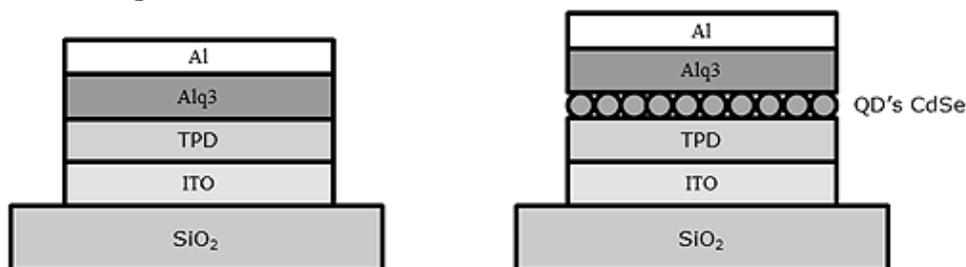


Figure 3. (a) Diagram of ITO/TPD/Alq3/Al OLED structure; (b) Diagram of ITO/TPD/Alq3/Al OLED structure, containing CQDs.

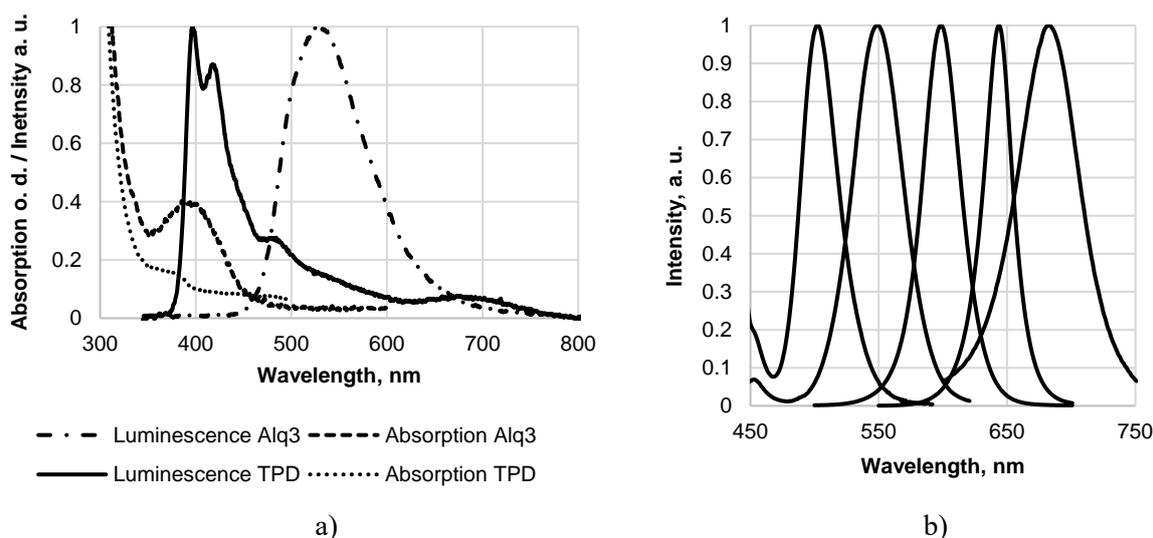


Figure 4. Absorption and luminescence spectra for organic layers in structure ITO/TPD/CQD/Alq3/Me (a) and luminescence spectra of arrays of colloidal quantum dots of various sizes (b)

In this paper we studied essential optical and electrical parameters of the created structures; thus, absorption and luminescence spectra of the structures and separate layers of TPD and Alq3 were examined. Absorption and luminescence structure layers charts shown in figure 4 a.

The luminescence spectrum of Alq3 was almost symmetrical with a strongly marked maxima at 530 nm and half-width of the spectral curve around 90 nm. There was also a peak of the absorption spectra at 390 nm. The luminescence spectrum of TPD was not symmetrical and had two local maxima at 400 and 420 nm. These spectra were in a good correlation with the data from third-party sources which allows the application of the vacuum thermal evaporation with a high speed of layer formation in the OLED technology. Adding to the array of colloidal quantum dots (Fig. 3b) changed band diagram of the structure, improving the collectability of the charge carriers in its active region. Current-voltage curves of the samples were obtained; rectifying effects were observed. Addition of the array of CdSe/ZnS CQDs is to allow the broadening of the luminescence spectrum to the wavelength of 680 nm, as well as the control over emission range of the structure (Fig. 4b).

Thus, arrays of CdS, CdSe/ZnS and CdSeZnS/ZnS colloidal quantum dots with peaks of photoluminescence in the range of wavelength from 400 to 680 nm were investigated. The luminescent organic ITO/TPD/Alq₃/Al structures and CdSe/ZnS quantum dots (QD) arrays were created. Electrical and optical properties of the samples were investigated. Fluorescent nanostructures with phosphors corresponding emission standards with color temperature of 5500 K and 6504 K and a CRI > 98 have been created.

4. Acknowledgements

The work was supported by the Ministry of Education of the Russian Federation in the framework of the project of the state task in the field of scientific activity, project number 16.1307.2014K.

5. References

- [1] Y Shirasaki, G Supran, M Bawendi. *Nature Photonics*, 2012, 7.
- [2] C Burda, S Link, M. Mohamed. 2001, *J. Phys. Chem. B* 105, 12286.
- [3] S Tarasov, O Aleksandrova, I Lamkin, A Maksimov, E Maraeva, I Mikhailov, V Moshnikov, S. Musikhin, S. Nalimova. *Semiconductors*, 2015, 49, 1710.
- [4] S. Tarasov, O. Aleksandrova, A. Maksimov, E. Maraeva, L. Matyushkin, V. Moshnikov, S. Musikhin. *Semiconductors*, 2014, 48, 13, 1729–1731.
- [5] I Mikhailov, S Tarasov, A Solomonov, L Matyushkin, D Mazing. *Functional materials*, 2014, 21, 2, 142-145.
- [6] I Mikhailov, S Tarasov, A Solomonov, O Aleksandrova, L Matyushkin, D Mazing. *Journal of Physics: Conference Series*, 2014, 572, 012029.
- [7] I Mikhailov, S Tarasov, I Lamkin, M Andreev, A Solomonov. *Journal of Physics: Conference Series*, 2015, 643, 012080.