Creation and investigation of OLED-structures with inclusion of colloidal quantum dots

Eremeev Mark Anatolyevich, Mikhailov I.I., Tarasov S.A., Lamkin I.A., Tadtaev P.O., Degterev A.E.
Saint Petersburg Electrotechnical University «LETI» (ETU), Saint-Petersburg, Russia
markeremeev22@gmail.com

Abstract. During the work organic light-emitting structures FTO/PEDOT:PSS//TPD/TPD+CQD CdSe(650)/Alq3/Al with an efficiency value of about 2% were created. The technique for introducing CdSe CQD (650) into the structure of OLED was developed. The change in the electroluminescence spectra in structures with colloidal quantum dots is demonstrated. The decrease in OLED switching on voltage in structures with the PEDOT: PSS layer is demonstrated.

1. Introduction

The creation and investigation of colloidal quantum dots (CQD) and devices based on them are some of the most perspective trends in modern electronics. At the same time, in recent years organic semiconductor materials and devices based on them (OLED) have become increasingly important, since their use makes it possible to create screens with low power consumption, high speed of operation, and intensive and rich color rendering [1]. The addition of CQD even to the simplest organic light-emitting structures should significantly improve their performance [2].

The typical structure of OLED consists of a transparent substrate, a transparent anode, two thin layers of organic compounds acting as transport layers for holes and electrons, respectively, and also a cathode [3]. More complex devices, characterized by improved characteristics, contain more layers [4]. For example, the application of the PEDOT:PSS hole-injecting layer allows to significantly reduce the switching on voltage of the structure, and the introduction into the structure of the TAZ material, which blocks holes and excitons, helps to highlight the emission peak of the active layer [5]. In recent years, studies have begun of organic light-emitting diodes that contain CQD acting as the active layer. Colloidal quantum dots encapsulated in the OLED structure allow to increase the efficiency of the device due to the high quantum yield of luminescence and make it possible to control the emission properties [6,7].

2. Experiment

2.1. Structures and methods of their creation

Various types of organic light-emitting diodes were created (Figure 1), some of which were encapsulated by CQD arrays. The structures consisted of a hole transport layer, which was TPD (N, N'-bis (3-methylphenyl) -N, N'-diphenylbenzidine) and PEDOT: PSS (poly (3,4-
ethylenedioxythiophene) -poly (styrene sulfonate) ), as well as an electronic transport layer of Alq3 (tris (8-hydroxyquinoline) aluminum) located between the aluminum cathode and the transparent anode of indium-tin oxide (ITO). The creation of OLED-structures was carried out by the methods of vacuum thermal evaporation and spin-coating.

The decision to use an additional of PEDOT:PSS layer despite a large number of studies of structures containing only powder materials [2, 5] is due to the more technologically simple application of PEDOT:PSS, and also to the improvement of the electrical parameters of the entire structure being created [1, 8]. As substrates were used glass 3x3 cm.

The main optical and electrical parameters of the structures were investigated: current-voltage and watt-ampere characteristics, efficiency characteristics of structures, as well as their luminescence spectra were obtained. The analysis of the current-voltage characteristics confirms the presence of the rectification effect in the created structures. The obtained luminescence spectra clearly demonstrate the possibility of changing the emission spectrum of OLED by introducing into the structure a layer of QCDs of different composition and sizes. This will allow without significant changes in the process technology to create devices with the necessary spectral characteristics and increased emission power.

Figure 1 shows that adding to the structure of the PEDOT:PSS layer allowed to reduce the OLED switching on voltage.

![Current-voltage characteristic of the ITO/TPD/Alq3/Al and ITO/PEDOT:PSS/TPD/Alq3/Al.](image)

**Figure 1.** Current-voltage characteristic of the ITO/TPD/Alq3/Al and ITO/PEDOT:PSS/TPD/Alq3/Al.

2.2. Samples characterization

Emitters containing CQD based on cadmium selenide coated with a wide-zone zinc sulphide shell were created in this work (Fig. 2). Figure 3 shows the photoluminescence spectrum of colloidal quantum dots CdSe/ZnS (650) and their image obtained using the method of scanning electron spectroscopy. This image was used to estimate the size of CQD. The possibility of changing the emission wavelength in the range of 500-650 nm due to the introduction of CdSe-based nanoparticles into the structure is shown (Fig. 4). An increase of the efficiency of OLED radiation was revealed when CQDs were introduced into them. The obtained efficiencies exceeded the value of 2%, which is
a rather high index for low-layer structures that do not contain dopants based on iridium. Further enhancement of efficiency of the created OLEDs and extension of the range of their radiation is discussed.

![Figure 2. Schematic representation of the organic light-emitting structures PEDOT:PSS/TPD/Alq3/Al and PEDOT:PSS/TPD/TPD+CQD_CdSe_650/Alq3/Al.](image)

To create these structures, methods of spin-coating and vacuum thermal deposition were used. The polymer compound PEDOT:PSS was applied to the ITO substrate by spin-coating. The time of spin-coating was 30 seconds, the speed was 3000 r/s, the number of layers was 2. The TPD + CQD_CdSe_650 layer was also applied by spin-coating. TPD and CQD were mixed in toluene. The spin-coating time was 30 seconds, the speed was 3000 r/s, the number of layers was 3. The layers TPD, Alq3 and aluminum contacts were made by the method of vacuum thermal evaporation.

![Figure 3. The photoluminescence spectrum of colloidal quantum dots CdSe/ZnS (650).](image)
Figure 4. Electroluminescence spectra of the organic structure containing colloidal quantum dots in the active layer.

The switching on voltage was 6 volts. This voltage is comparable with the voltage of inclusion of similar organic structures [8]. The presence of a "bulge" on the current-voltage characteristic in the vicinity of 6 volts is explained by the formation of current-conducting shunt channels (Fig. 5). These channels are formed due to the presence of unevenness on the surface of the layers. As a result, regions with small thicknesses of layers appear which, when the structure is first switched on, "break through" and become conductive channels that are not involved in the electroluminescence process. To eliminate irregularities on the surface of the layers, work is underway to improve the technology of creating organic structures.

Figure 6 shows the watt-ampere characteristics of created structures. It shows that in a sample with a CQD, the optical power for the same current is lower, this is due to the additional expenditure of energy to excite radiation in the CQD layer. The shapes of both characteristics are similar to those of the watt-ampere characteristics of inorganic light-emitting diodes.
Figure 5. The current-voltage characteristic of the ITO/PEDOT:PSS/TPD/TPD+CQD_CdSe_650/Alq3/Al structure.

Figure 6. Watt-ampere characteristic of the ITO/PEDOT:PSS/TPD/Alq3/Al structure and the ITO/PEDOT:PSS/TPD/TPD+CQD_CdSe_650/Alq3/Al structure.

3. Conclusions

The technology of creating OLED structure FTO/PEDOT:PSS/TPD/Alq3/Al was developed by methods of spin-coating and vacuum thermal evaporation. It is shown that adding to the structure of the PEDOT:PSS layer allowed to reduce the OLED switching on voltage. A technique for introducing CdSe CQD (650) into the OLED structure was developed. An increase of the efficiency of OLED radiation is shown when introducing CQD into them. The obtained efficiencies exceeded the value of
2%, which is a rather high index for structures based on FTO/PEDOT:PSS//TPD/TPD+CQD CdSe (650)/Alq3/Al, which do not contain dopants based on iridium.

At present, work is under way to increase the brightness of the radiation from the CQD array due to the optimization of the procedure for the distribution of quantum dots in the structure. Preliminary work is being done to introduce into the composition of the structure a multicomponent CQD array of different composition and size, having a predetermined PL spectrum [9, 10]. The use of such arrays will make it possible to create organic structures with an EL spectrum that is close to the solar emission spectrum with a color rendering index of CRI above 95 or with any other form of the emission spectrum.

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References
[1] K. S. Cho, E. K. Lee, W. J. Joo, E. Jang, T. H. Kim, S. J. Lee, S. J. Kwon, J. Y. Han, B. K. Kim, B. L. Choi, and J. M. Kim, Nature Photon. 3, 341 (2009).https://doi.org/10.1038/nphoton.2009.92
[2] V. L. Colvin, M. C. Schlamp, and A. P. Alivisatos, Nature 370, 354 (1994).https://doi.org/10.1038/370354a0
[3] Y. Karzazi // Organic Light Emitting Diodes: Devices and applications // J. Mater. Environ. Sci. 5 (1) (2014) 1-12.
[4] E. M. Stepanov, I. I. Mikhailov, S. A. Tarasov, A. V. Solomonov, Proceedings of the 2016 IEEE North West Russia Section Young Researchers in Electrical and Electronic Engineering Conference, EIConRusNW, 82 – 84, (2016);
[5] S. Coe, K. W. Woo, M. G. Bawendi, and V. Bulovic, Nature 420, 800 (2002).https://doi.org/10.1038/nature01217
[6] Fengjuan Zhang, Shujie Wang, Lei Wang // Nanoscale. 2016. V. 8. P. 12182–12188. doi: 10.1039/C6NR02922A
[7] Mikhailov I.I., Tarasov S.A., Lamkin I.A., Tadtaev P.O., Kozlovich L.I., Solomonov A.V., Stepanov E.M. // J. Phys. Conf. Ser. 2016. V. 741. P. 012103.
[8] N. S. Kurochkin, A. A. Vashchenko, A. G. Vitukhnovsky, P. N. Tananaev // Effect of the Length of Ligands Passivating Quantum Dots on the Electrooptical Characteristics of Organic Light Emitting Diodes // ISSN 10637826, Semiconductors, 2015, Vol. 49, No. 7, pp. 953–958.
[9] P. O. Tadtaev, M. O. Gurevich ; L. I. Kozlovich ; I. I. Mikhailov The study of CdSe/ZnS and CdSe/ZnS/ZnS colloidal quantum dots structures as flexible electronics components // IEEE. – 2016. 10.1109/EIConRusNW.2016.7448126, 85-87.
[10] E. M. Stepanov; I. I. Mikhailov; S. A. Tarasov; A. V. Solomonov Light-emitting structures based on colloidal quantum dots of cadmium sulphide having a high color rendering index // IEEE. – 2016. 10.1109/EIConRusNW.2016.7448125, 82-84.