Effect of surface ligands on the performance of organic light-emitting diodes containing quantum dots

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ABSTRACT

Quantum dots (QDs) have numerous applications in optoelectronics due to their unique optical properties. Novel hybrid organic light-emitting diodes (OLEDs) containing QDs as an active emissive layer are being extensively developed. The performance of QD–OLED depends on the charge transport properties of the active layer and the degree of localization of electrons and holes in QDs. Therefore, the type and the density of the ligands on the QD surface are very important.

We have fabricated OLEDs with a CdSe/ZnS QD active layer. These OLEDs contain hole and electron injection layers consisting of poly(9-vinyl carbazole) and ZnO nanoparticles, respectively. The energy levels of these materials ensure efficient injection of charge carriers into the QD emissive layer.

In order to enhance the charge transfer to the active QD layer and thereby increase the OLED efficiency, the QD surface ligands (tri-n-octyl phosphine oxide, TOPO) were replaced with a series of aromatic amines and thiols. The substituents were expected to enhance the charge carrier mobility in the QD layer. Surprisingly, the devices based on the original TOPO-coated QDs were found to have the best performance, with a maximum brightness of 2400 Cd/m^2 at 10 V. We assume that this was due to a decrease in the charge localization within QDs when aromatic ligands are used. We conclude that the surface ligands considerably affect the performance of QD–OLEDs, efficient charge localization in QD cores being more important for good performance than a high charge transfer rate.

Keywords: organic light-emitting diodes, electroluminescence, quantum dots, CdSe/ZnS

1. INTRODUCTION

Semiconductor quantum dots (QDs) obtained by means of colloidal synthesis are increasingly widely used in designing light-emitting devices. These QDs have a wide absorption spectrum and a narrow luminescence spectrum (about 45–30 nm) whose position is easily tunable by varying the QD size. The luminescence quantum yield of the best QD samples obtained to date is more than 90% [1, 2–5]. In addition, QDs are exceptionally photostable compared to organic luminophores [6]. CdSe is the most popular material for QDs emitting in the visible range.

Two main types of light-emitting devices employing QDs are currently being developed. The first are down-conversion devices, in particular, "white" light-emitting diodes. Devices of the second type are hybrid organic light-emitting diodes (OLEDs) with the active electroluminescent layer consisting of QDs. When nanoparticles are used to form the active layer of a light-emitting diode, they are located at the interface between the electron and hole transport layers. The width of the QD film varies from one to several monolayers. Most OLEDs developed employ core/shell QDs with type I heterojunction (e.g., CdSe/ZnS). The QD shell should have a wide band gap to enhance the localization of charge carriers in the QD level and suppress nonradiative recombination of excitons.

In addition to the QD structure, the performance of hybrid OLEDs depends on the type of QD surface ligands. The ligands are used to prevent QD aggregation at the stage of synthesis. In the light-emitting layer of hybrid OLEDs, the ligands fulfill two functions. First, they separate QDs from one another, thereby enhancing the localization of the

injected electrons and holes and facilitating their radiative recombination. On the other hand, ligands with long alkyl chains form an insulating layer on the QD surface that prevents efficient injection of charges. This raises the problem of optimizing the type of QD surface ligands. For solving this problem, we fabricated hybrid OLEDs based on CdSe/ZnS QDs with different types of surface ligands and studied their electroluminescent characteristics.

2. EXPERIMENTAL

1.1 Materials

Cadmium oxide (powder, 99.5%), zinc oxide (powder, 99.99% trace metals basis), 1-octadecene (ODE, technical grade, 90%), oleylamine (OLA, technical grade, 70%), selenium (powder, 100 mesh, 99.5%), thiourea (ACS reagent, ≥99.0%) tri-*n*-octylphosphine (TOP, technical grade, 97%), tri-*n*-octylphosphine oxide (TOPO, reagent grade, 99%), 2-ethylhexanoic acid (2-EHA, 99%), tri-*n*-octylamine (TOA, 98%), triethylene glycol dimethyl ether (TEGDME, ReagentPlus, 99%), tetraethyl ammonium bromide (TEABr, ReagentPlus®, 99%), sodium hydroxide (BioXtra, ≥98%), aniline (Ani, ACS reagent, ≥99.5%), thiophenol (TP, ≥99%) and anhydrous solvents (chloroform, hexane, *o*-xylene, methanol, acetone, *n*-butanol, 2-propanol, and DMSO) were purchased from Sigma-Aldrich; *n*-hexadecylphosphonic acid (HDPA, 97%) was purchased from PlasmaChem GmbH. All chemicals were used as received without purification.

1.2 Synthesis of CdSe/ZnS quantum dots

The procedure for synthesis of QDs was adapted from [7]. A mixture of 1 mmol of CdO, 2.5 mmol of 2-ethylhexanoic acid, and 2 ml of ODE was heated to 220°C in argon atmosphere in a 25-ml three-necked flask until complete dissolution of cadmium oxide. After cooling of the flask to room temperature, 6 ml of ODE, 0.5 mmol of HDPA, and 2 ml of TOA were added, and the mixture was degassed at 120°C under a pressure of 5 mbar for 25 min. The Cd precursor solution was slowly heated to 300°C in argon atmosphere during 1 h while the selenium precursor solution was being prepared. Selenium powder (2 mmol), 0.5 ml of ODE, and 2 ml of TOP were placed in a glass test tube and intensely purged with argon. The obtained solution of TOPSe was collected into a 5-ml syringe and rapidly injected into the cadmium precursor solution, kept at 300°C under vigorous stirring. The formation of CdSe core nanocrystals was initiated immediately, The core nanocrystals reached a size of 2.9 nm within 3 min, and the reaction was stopped by intense cooling of the flask with an air flow. The CdSe cores were precipitated from crude solution using isopropyl alcohol and then sedimented by centrifugation at 5000 rpm for 5 min. Successive redissolution/precipitation of the CdSe cores was performed twice using chloroform/methanol as the solvent/coagulant combination, respectively.

The purified 2.9-nm CdSe cores were redispersed in a mixture of 6 ml of ODE and 6 ml of OLA to grow a shell on their surface. After degassing of the mixture at 100°C for 25 min, 1 ml of TOP was injected into the flask, and the core solution was gradually heated to 170°C in argon atmosphere. The shell precursor solution (a mixture of previously prepared solutions of 3 mmol of zinc 2-ethylheanoate and 3 mmol of thiourea diluted to a total volume of 6 ml with TEGDME) was slowly injected at 150°C using a syringe pump at a rate of 6 ml/h. After the injection of the shell precursors, the reaction mixture was kept at 170°C for an additional 20 min to ensure complete transformation of the precursors, and the mixture was cooled down to room temperature. The isolation and purification of core–shell QDs was performed similarly to these procedures for core nanocrystals. After the final centrifugation step, the QDs were dispersed in 5 ml of chloroform.

1.3 Surface modification of CdSe/ZnS quantum dots

The solution of purified CdSe/ZnS QDs, with oleylamine molecules as native surface ligands, was divided into five equal parts, and a chloroform solution containing an excess amount of new surface ligands (about 1000 ligand molecules per QD) was added to each portion. The solutions were incubated at room temperature for 24 h and then precipitated by addition of methanol. After centrifugation, the QDs were redispersed in chloroform, a new portion of ligand solution was added, and incubation was repeated. After the second precipitation by methanol and centrifugation, purified QDs with new surface ligands were dispersed in *o*-xylene for further processing.

1.4 Synthesis of ZnO nanocrystals

ZnO nanoparticles were synthesized according to a previously reported procedure. Zinc acetate dihydrate (3 mmol) was dissolved in 30 ml of DMSO for 1 h at room temperature. During this procedure, a fresh solution of tetraethyl ammonium hydroxide (TEAH) was prepared by mixing equimolar amounts of TEABr and NaOH solutions in methanol. This solution was filtered through a 220-nm syringe filter and diluted to obtain 10 ml of a 0.1 M solution of TEAH in

methanol. This solution was added dropwise to an intensely stirred solution of zinc acetate in DMSO for 1.5 min; then, the mixture was incubated while stirring at room temperature for 1 h. The resultant opalescent solution of ZnO nanoparticles in DMSO was precipitated by excess volume of acetone, centrifuged, and redispersed in an ethanol–*n*-butanol (1:1) mixture to a concentration of 20 mg/ml.

1.3. Fabrication of QD–OLEDs

A patterned ITO glass substrate was cleaned in an ultrasonic bath sequentially with detergent, deionized water, isopropanol and then, finally oxygen plasma treated for 2.5 min. First, a hole injection layer (HIL) of PEDOT:PSS was spin-coated at 2000 rpm for 60 s and baked at 150°C for 30 min in an Ar-filled glovebox. After that, a hole transport layer (HTL) of PVK was applied onto the HIL from a 10-mg/ml solution in chlorobenzene using the same spin-coating and baking procedures. QDs were dispersed in *o*-xylene to a concentration of ~20 mg/ml, and an emission layer (EML) of CdZnS/ZnS QDs was spin-deposited at 2000 rpm for 20 s (without subsequent baking). The EML was spin-coated with ZnO nanoparticles from a transparent ethanol–*n*-butanol solution (~20 mg/ml) at 1000 rpm for 60 s; this was followed by baking at 60°C for 30 min in the same glovebox. Finally, a 0.9-nm-thick LiF and a 100-nm-thick Al layers of the cathode were thermally evaporated onto the electron transport layers (ETLs) to complete the ITO/PEDOT:PSS/PVK/(CdZnS/ZnS)/ZnO/LiF/Al multilayered structure.
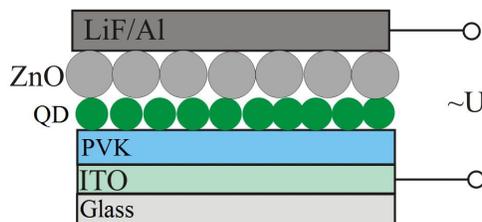

Fig. 1. The schematic structure of the QD–OLED device.

1.4. Instruments and methods

The growth of QDs was monitored using an Agilent Cary 60 UV-Vis spectrophotometer and an Agilent Cary Eclipse spectrofluorimeter. The photoluminescence quantum yield (PL QY) of the QDs was determined using methanolic solution of Rhodamine 6G as a reference dye with the known PL QY of 95%. TEM and DF-STEM imaging of QDs was performed on a JEOL JEM-2100F microscope operating at 200 kV. TEM samples were prepared by drop-casting of 5 μl of a purified QD solution in toluene onto a 200-mesh carbon-coated copper grid and drying it under ambient conditions. Processing of TEM images was performed using the ImageJ software [8].

3.   RESULTS AND DISCUSSION

Efficient injection of charge carriers from the anode or cathode into QDs is crucial for QD–OLED performance. Therefore, the selection of organic semiconductors according to their energy levels relative to those of QDs is of special importance. The organic semiconductors TPBi and Alq$_3$ [9] are widely used in OLEDs; however, they fall behind the inorganic semiconductors ZnO and TiO$_2$ as components of ETLs, because the latter are more resistant to moisture and oxygen and, which is more important, more efficiently inject electrons [10,11]. In these devices, QDs are usually excited through direct injection of carriers [12]. Therefore, one of the most important problems in developing these systems is proper selection of the relative positions of the energy levels of the components. Poly-TPD usually serves as a material for the HTL, because it is highly resistant to solvents commonly used for dissolving QDs (e.g., chloroform and toluene) [13]. However, the quantum efficiency of QD–OLEDs strongly depends on the injection of holes from the HIL into QDs. Therefore, we used PVK, because its hole energy level (–5.8 eV) is lower than that of poly-TPD (–5.2 eV), and, hence, it can more efficiently inject holes into QDs. In addition, PVK is less expensive than poly-TPD.

The quality of the CdSe/ZnS QD active layer is another important factor. This quality strongly depends on the solvent from which the layer is deposited. For example, comparative studies have shown that *o*-xylene is preferable over hexane, because the QD film deposited from a hexane solution is optically heterogeneous.

Note that the originally high PL QY of QDs drastically decreased upon formation of solid-state films, because they were purified of surfactants [14]. Surfactants are routinely used for preventing aggregation in the course of nanocrystal

growth. Traditionally, surfactants with long alkyl chains, such as oleic acid (OA) and TOPO, are used for this purpose. They form am electrically insulating layer preventing efficient charge transfer from the polymer to the QDs, as well as electron transfer between QDs. For example, the charge carrier mobility is 10^{-5} cm^2/V*s in a film of CdSe QDs coated with TOPO and 10^{-2} cm^2/V*s in bulk CdSe. In order to solve this problem, we studied the dependence of the current density–voltage and luminance–voltage characteristics of QD–OLEDs on the type of surfactant coating the QDs.
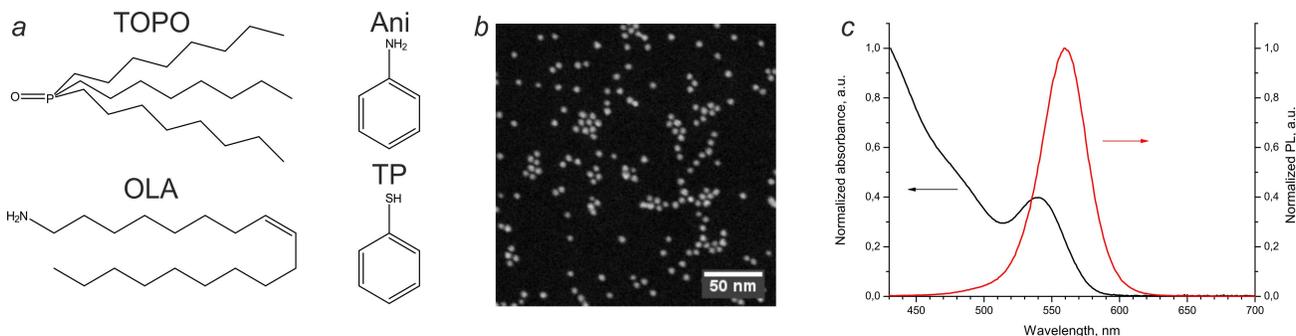

Fig. 2. (*a*) Chemical structures of QD surface ligands used in this study: TOPO, tri-*n*-octylphosphine oxide; OLA, oleylamine; Ani, aniline; TP, thiophenol. (*b*) A DF-STEM image of as-prepared CdSe/ZnS QDs prior to ligand exchange. (*c*) The absorbance and photoluminescence spectra of as-prepared CdSe/ZnS QDs.

When forming films of CdSe/ZnS QDs coated with different surfactants, one can control their conductance not only because different surfactants have different conductances, but because their molecules are of different lengths; hence, the distances between QDs coated with them are also different. For example, the TOPO molecule is about 0.8 nm in length; i.e., it is two times longer than the aniline and thiophenol molecules (which are of about the same size) and two times shorter than the oleylamine molecule. Thus, if a film is formed out of QDs with the minimum necessary amount of surfactant, the film of CdSe/ZnS QDs with oleylamine ligands will be the least dense and that of QDs with aromatic ligands will be the most densely packed. Figure 2a shows the chemical structures of QD surface ligands used in this study.

Figure 3 shows the current density–voltage and luminance–voltage characteristics of four devices containing an active (emitting) layer of CdSe/ZnS QDs with different surfactants. The surfactants may be divided into two groups: aromatic ones with a system of conjugated π-electrons and aliphatic ones. As can be seen in the plots, the QD–OLED devices employing aliphatic surfactants (TOPO and oleylamine) had the best performance characteristics. For example, at a voltage of 10 V and a current density of 600 mA/cm^2, brightnesses of 1700 and 2400 cd/m^2 were obtained in the cases of CdSe/ZnS QDs coated with oleylamine and TOPO, respectively. The brightnesses of the other devices did not exceed 1200 cd/m^2. Low brightnesses of the devices employing aromatic surfactants (thiophenol and aniline) may have been related to the small distances between QDs and a relatively high conductance of the surfactants themselves due to the system of conjugated π-electrons. Both factors facilitate charge delocalization, which hinders radiative recombination.
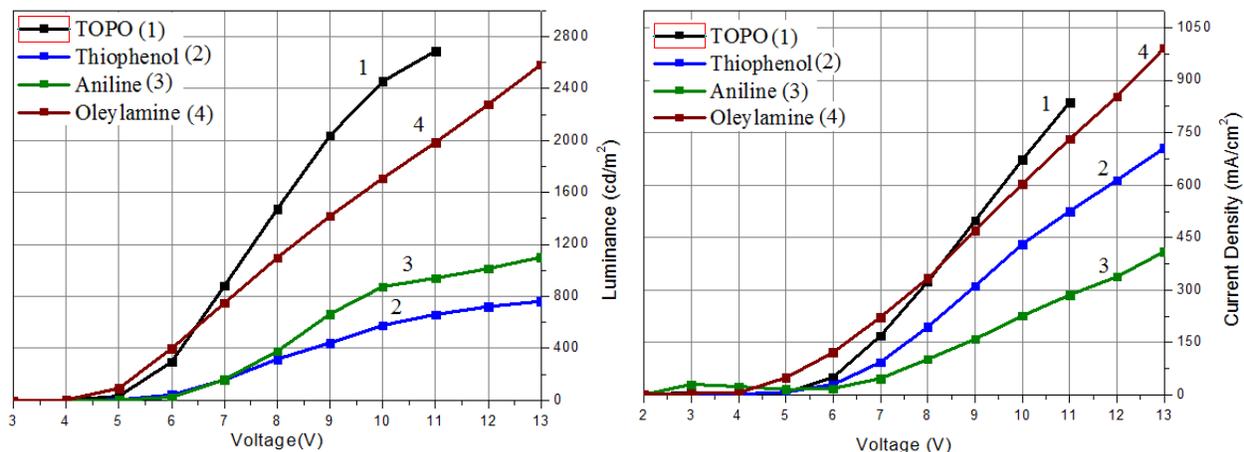
Fig. 3. (a) Current density–voltage characteristics and (b) luminance–voltage characteristics of QD–OLEDs as dependent on the surfactants on the CdSe/ZnS QD surface.

Figure 3a shows the photoluminescence (PL) spectrum of a CdSe/ZnS QD solution and the electroluminescence (EL) spectrum of a QD–OLED. As seen in the figure, the maximums and widths of these spectra are practically the same (~570 arbitrary units and 40 nm, respectively). This suggests efficient suppression of Förster resonance energy transfer (FRET) often occurring in QD films. The corresponding Commission Internationale de l'Eclairage (CIE) color coordinates of the orange emission spectra (0.450 and 0.545) are shown in Figure 3b.
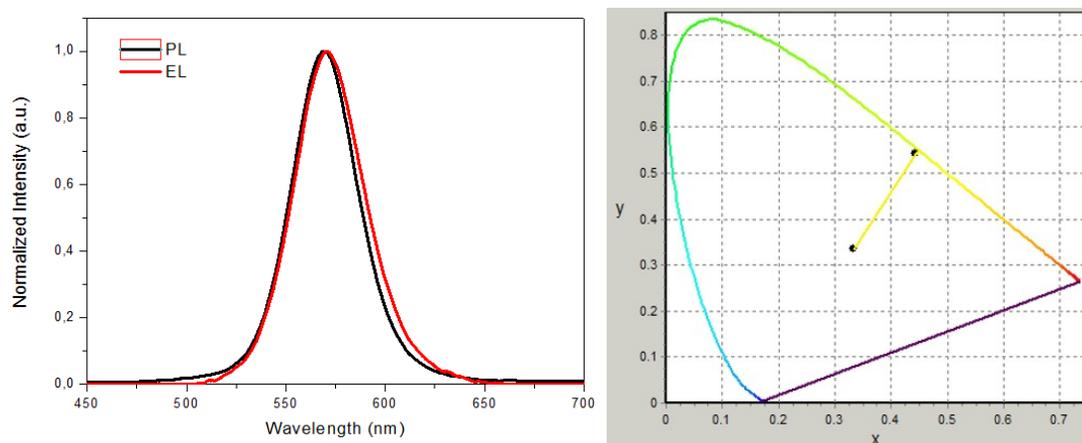

Fig. 4. (a) Comparison of the PL spectrum of a QD solution and the EL spectrum of a QD–LED. (b) The corresponding CIE color coordinates (0.450 and 0.545).

Thus, we have performed the first comparison of QD–OLEDs whose active layer is formed by CdSe/ZnS QDs with different surfactants and demonstrated that the devices employing CdSe/ZnS QDs with oleylamine and TOPO as surfactants exhibit the best performance. The maximum brightness of such a QD–OLED device is 2400 cd/m^2, and its maximum light efficiency is 0.383 lm/W. Further optimization of the widths of QD–OLED layers is likely to further improve the performance of QD–OLEDs.

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