

Cadmium-free quantum dot light emitting devices: energy-transfer realizing pure blue emission

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In this study, deep blue, pure electroluminescence (EL) at 441.5 nm from a ZnSe/ZnS quantum dot light-emitting device (QD-LED) is obtained by using poly (4-butylphenyl-diphenyl-amine) (poly-TPD) as the hole-transport layer (HTL) to open up the channel for energy transfer from poly-TPD to QDs. The emission originating from HTL is observed in the QD-LED with *N,N'*-bis (tolyl)-*N,N'*-diphenyl-1,1'-biphenyl-4,4'-diamine functionalized with two styryl groups (2-TPD) as the HTL due to inefficient energy-transfer from 2-TPD to QDs. The poly-TPD based device exhibits color-saturated blue emission with a narrow spectral bandwidth of full width at half maximum (~17.2 nm). These results explore the operating mechanism of the QD EL and signify a remarkable progress in deep blue QD-LEDs based on environmental-friendly QD materials. © 2012 Optical Society of America

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Colloidal quantum dots (QDs), due to the unique optoelectronic properties and high emission quantum yield obtained by adjusting their size and composition, have been extensively investigated for potential applications in full-color flat-panel displays or as low power consumption solid-state lighting sources [1]. Colloidal QD light emitting devices (QD-LEDs) possess promising features of a much wider color gamut than current displays, such as liquid crystal displays or organic light emitting devices [2], due to the narrow emission of monodisperse QDs [full width at half-maximum (FWHM) <30 nm] as well as their tunable emissions in the full visible range. Moreover, the QDs can be dispersed in common solvents enabling solution process, which has been widely used in many of optoelectronic devices.

Most QD-LEDs with narrow emissions currently reported are based on cadmium-containing QDs (CdSe, CdS, and CdTe, etc.) which are of environmental and cost concern. The heavy-metal nature of cadmium composition raises concerns about carcinogenicity and other chronic health risks as well as disposal hazards [2]. Fortunately, a broad range of compound and elemental semiconductors, including InP, Si, ZnSe, and ZnCuInS have been exploited to design and synthesize colloidal QDs, which are more environmentally friendly and have also been used in QD-LEDs [3–8]. Especially, blue QD based LEDs have already been reported [6,7], which is crucial to achieving a full color display. However, electroluminescence (EL) of the blue devices is accompanied with a deep trap emission in longer wavelength ranges, and the efficiency is much lower than that of the red and green QD based devices [9–16]. It is particularly desirable to explore the operating mechanism for improvement in the performance of blue LEDs.

In this study, we report deep blue QD-LEDs based on ZnSe/ZnS core/shell QDs as the emitter with an EL emission wavelength of 441.5 nm. The operating mechanism of the QD EL in the blue devices is studied by utilizing different hole-transport layers (HTLs), poly (4-butylphenyl-diphenyl-amine) (poly-TPD), and *N,N'*-bis (tolyl)-*N,*

N'-diphenyl-1, 1'-biphenyl-4, 4'-diamine functionalized with two styryl groups (2-TPD). The poly-TPD is closely related to the 2-TPD, which has almost the same highest occupied molecular orbital (HOMO). Energy-transfer (ET) is demonstrated to be the dominant operating mechanism in the poly-TPD based blue device.

The QD-LEDs consisted of glass substrate coated with ITO/*MoO*₃ (12 nm)/HTL (40 nm)/QDs (2–3 monolayers)/TPBi (40 nm)/LiF (1 nm)/Al (200 nm). The ITO glass substrates were cleaned in ultrasonic bath with isopropyl alcohol, acetone, and methanol sequentially. The *MoO*₃ layer was first deposited by thermal evaporation at a rate of 0.05 nm/s. For device A, the poly-TPD layer was spin-coated onto the *MoO*₃ layer at 1600 rpm for 1 min from a 0.5 wt. % chlorobenzene solution to give a homogeneous layer of 40 nm. Then, this film was dried at 100°C in a glove box (MBRAUN) for 30 min. For device B, the 2-TPD layer was spin coated onto the *MoO*₃ layer at 1600 rpm for 1 min from a 0.5 wt. % chlorobenzene solution to obtain a homogeneous layer of 40 nm. This film was crosslinked at 180°C in the same glove box for 30 min. The ZnSe/ZnS core/shell QDs used for QD-LEDs here was synthesized according to the previously published method with a diameter of ~9.6 nm [17]. QD toluene solution [optical density (OD) is 1.8 at the wavelength of 400 nm] was deposited on poly-TPD and 2-TPD films, respectively, by spin-coating at 1200 rpm for 1 min. Then, TPBi, LiF, and Al were successively evaporated onto the top of HTLs at a rate of 0.2, 0.01, and 0.5 nm/s, respectively, under a base pressure of 4×10^{-6} Torr. The layer thickness and the deposition rate of the materials were monitored *in situ*. The characteristics of current–voltage–luminance and EL spectra were measured by a programmable Keithley model 2400 power supply and a Photo-research PR655 spectrometer in air at room temperature and no external package for devices. The morphology of QD films was characterized with scanning electron microscope (SEM, Hitachi S4800). The photoluminescence (PL) spectrum was measured by a Hitachi F-4500 spectrophotometer.

The SEM images of ZnSe/ZnS QDs spin-coated on the poly-TPD are shown in Fig. 1. As can be seen, a high quality close-packed QD film with very few cracks and voids is obtained, which is a crucial factor in fabricating efficient QD-LEDs. The QD film possessing the same characteristics is also obtained on the 2-TPD film and the data is not shown here. The average diameter of ZnSe/ZnS QD was estimated to be ~ 9.6 nm. The particle size distribution is very narrow, which is also demonstrated by a narrow PL spectrum and first excitonic absorption peak as seen in Figs. 2(a) and 2(c).

Fig. 2(a) shows the EL spectra of devices A and B at voltage of 5 V and the PL spectrum of ZnSe/ZnS QDs in toluene at the excitation wavelength of 350 nm. A strong emission from 480 to 700 nm is observed in device B with 2-TPD as the HTL. In contrast, a nearly pure QD emission with a narrow spectral bandwidth (FWHM ~ 17.2 nm) is obtained for the poly-TPD based device. As we know, two mechanisms have been proposed to explain EL of QD-LEDs [18,19]. By the first mechanism, charge carriers transported through organic/inorganic charge-transport layers are directly injected into QDs, resulting in formation of excitons that can radiatively recombine. The second mechanism depends on the ability to form excitons on the organic molecules surrounding the QD film. Then the excitons transfer energy to the QDs. Here, the first operating mechanism of QD-LEDs is called carrier-injection-type and the second one is called ET-type. In general, both mechanisms exist in the devices. However, one may play a dominant role. It is desirable to explore the operating mechanism and explain the difference in EL data between devices A and B. For this purpose, we fabricated devices with a structure of glass/ITO/MoO₃ (12 nm)/poly-TPD or 2-TPD (50 nm)/TPBi (45 nm)/LiF (1 nm)/Al (200 nm). All the films were fabricated using the same technique described above.

The energy-level diagram of the materials used in this work is shown in Fig. 2(b). The HOMO and lowest unoccupied molecule orbital (LUMO) energy levels are cited from the literature [3,20,21]. The band-edge of the QDs is determined from the optical band gap from Fig. 2(c), which is in accordance with effective mass approximation calculations [22]. The HOMO energy level of poly-TPD is nearly the same as that of 2-TPD, indicating that they have similar hole-injection barrier to QDs, i.e., the ability of hole-injection from both HTLs to QDs is almost the same. This result indicates that the difference between EL spectra of devices A and B does not originate from hole-injection.

The EL spectra from poly-TPD and 2-TPD and the absorption spectrum of ZnSe/ZnS QDs in toluene are

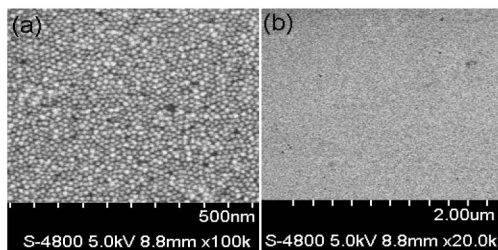


Fig. 1. SEM images of ZnSe/ZnS QDs spin-coated on the poly-TPD film for (a) high and (b) low resolution.

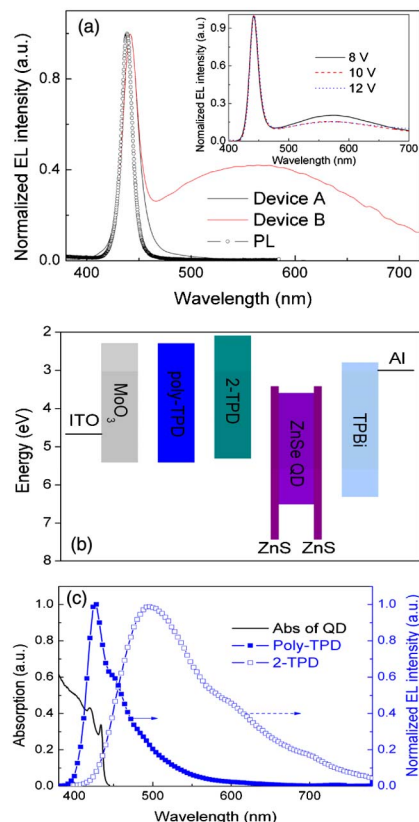


Fig. 2. (Color online) (a) EL spectra of ZnSe/ZnS QD-LEDs with different HTLs and the PL spectrum of the QDs in toluene. Inset shows the EL spectra of device B at different voltage. (b) Energy-level diagram of the materials used in our work. (c) Absorption spectrum of the QDs and EL spectra from poly-TPD and 2-TPD.

shown in Fig. 2(c). There is much difference between the EL spectra from poly-TPD and 2-TPD. It was reported that the PL of cross-linked 2-TPD near the band edge was completely quenched after a curing process, while a weak and broad PL band peaked at a wavelength of 500 nm was observed [21]. We also observed the broad emission originating from 2-TPD in device B, which is similar to the PL of 2-TPD film. We can see there is a larger spectral overlap between the poly-TPD emission and QD absorption than between the 2-TPD emission and QD absorption. In our devices, excitons are formed at the HTL/QD interface. Due to the higher potential barrier (>2 eV) for hole injection from both HTLs into QDs, as compared to the potential barrier (<1.5 eV) for electron injection from the QDs into HTLs, the majority of excitons are formed on HTL molecules. Therefore, efficient ET is necessary to obtain strong or pure EL emission from QDs. Notably excitons formed on poly-TPD molecules can efficiently transfer energy to the QDs via the Förster mechanism [23] because of the large spectral overlap between the QD absorption and poly-TPD emission. Conversely, the ET is inefficient from 2-TPD to the QDs due to the little spectral overlap. The inset of Fig. 2(a) shows the EL spectra of device B at voltage of 8, 10, and 12 V. We can see that the ratio of emission intensity of 2-TPD to QDs increases from 8 to 10 V and is almost the same at 10 and 12 V, which means that the

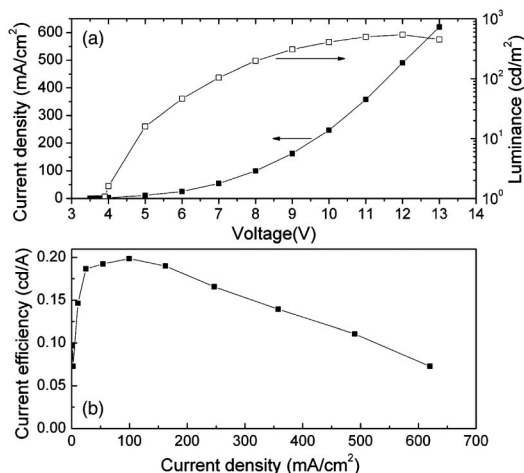


Fig. 3. (a) Current density–voltage–luminance. (b) Current density–efficiency curves of device A.

probability of hole injection into QDs is increased with increasing operation voltage and keeps nearly constant for the voltage more than 10 V. Consequently, we consider that the dominant operating mechanism of QD EL is ET-type in device A, and carrier-injection-type in device B. Here, it is valuable to note that very small contribution to the EL from poly-TPD in device A is also observed, which is ascribed to the incomplete ET from the poly-TPD to the QDs due to the emission from the poly-TPD at long wavelength range near 500 nm. However, by using two different HTLs, we show that two mechanisms of QD EL can operate in such blue devices with one of them being dominant one. We believe that a more efficient and pure blue QD-LED based on ZnSe/ZnS QDs can be achieved by utilizing hole-transport materials with larger band gap and lower HOMO energy level to enhance the ET efficiency and charge injection.

The current density–voltage–luminance curves of device A are shown in Fig. 3(a). The turn-on voltage (the voltage when the luminance is 1 cd/m^2) is 3.9 V and the maximum luminance is 542.1 cd/m^2 . The current density–efficiency curve for device A is shown in Fig. 3(b). The peak current efficiency is 0.20 cd/A at current density of 100 mA/cm^2 .

In summary, we fabricated deep blue QD-LEDs using ZnSe/ZnS QDs as the emitter. The operating mechanism of the blue devices was investigated. We found that the ET played a dominant role in the QD EL of the poly-TPD based devices. The utilization of poly-TPD as the HTL opened up the channel for the ET from poly-TPD to QDs, resulted in extremely narrow EL (FWHM $\sim 17.2 \text{ nm}$) and high color purity blue emission with a peak current

efficiency of 0.20 cd/A. This work demonstrated the potentiality of ZnSe/ZnS QDs as blue emitters in QD-LEDs to obtain pure QD EL without emission from organic materials and deep traps.

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