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# Cadmium-free quantum dots based violet light-emitting diodes: High-efficiency and brightness via optimization of organic hole transport layers

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## ABSTRACT

Bright and efficient violet quantum dot (QD) based light-emitting diodes (QD-LEDs) with heavy-metal-free ZnSe/ZnS have been demonstrated by choosing different hole transport layers, including poly(4-butyl-phenyl-diphenyl-amine) (poly-TPD), poly[9,9-dioctylfluorene-co-N-[4-(3-methylpropyl)]-diphenylamine] (TFB), and poly-N-vinylcarbazole (PVK). Violet QD-LEDs with maximum luminance of about 930 cd/m$^2$, the maximum current efficiency of 0.18 cd/A, and the peak EQE of 1.02% when poly-TPD was used as HTL. Higher brightness and low turn-on voltage (3.8 V) violet QD-LEDs could be fabricated when TFB was used as hole transport material. Although the maximum luminance could reach up to 2691 cd/m$^2$, the devices exhibited only low current efficiency (~0.51 cd/A) and EQE (~2.88%). If PVK is used as hole transport material, highly efficient violet QD-LEDs can be fabricated with lower maximum luminance and higher turn-on voltages compared with counterpart using TFB. Therefore, TFB and PVK mixture in a certain proportion has been used as HTL, turn-on voltage, brightness, and efficiency all have been improved greatly. The QD-LEDs is fabricated with 7.39% of EQE and 2856 cd/m$^2$ of maximum brightness with narrow FWHM less than 21 nm. These results represent significant improvements in the performance of heavy-metal-free violet QD-LEDs in terms of efficiency, brightness, and color purity.

## 1. Introduction

With the fast development of inorganic semiconductor quantum dots (QDs), high quantum efficiency (with quantum yields (QYs) >80%), high color purity, high stability, low-cost, and scalable production of QDs has been established for the further researches towards many important applications [1–8]. Quantum dot-based light-emitting diodes (QD-LEDs) which generate electroluminescence by using electric current to directly excite QDs represent the next step in the utilization of QDs for light-emitting technologies. Most of the researches about QD-LEDs have focused on the Cd-based QDs, because of their high emission efficiency and size-tuned photoluminescence (PL) in the visible range [9–15]. Such as, for the Cd-based red emitting QD-LEDs, the external quantum efficiency (EQE) which is directly proportional to power conversion efficiency and is therefore a key metric for solid-state lighting and displays can reach as high as 18%, with maximum luminance up to 50,000 cd/m$^2$ [15]; for green emitting devices, Kwak et al. [12] demonstrated QD-LEDs with maximum brightness and EQE of 218,800 cd/m$^{-2}$ and 5.8%, respectively; even for the blue emitting QD-LEDs, we note that Lee et al. recently recorded peak EQE as high as 7.1% [16]. But for the good monochromaticity heavy-metal-free QD based LEDs, most of the researches have focused on InP/ZnS QDs based LEDs [17–19]. Currently, the results of the heavy-metal-free QD-LEDs have recorded 3.46% of EQE and 3900 cd/m$^2$ of maximum brightness [19]. However, no matter heavy-metal-contained QDs or heavy-metal-free QDs, all have been absent from the fabrication of highly efficient and bright violet-emitting QD-LEDs.

For now, the studies of violet Cd-free QD-LEDs are mainly concentrated on the ZnSe-based QDs since ZnSe has a bulk band gap of 2.7 eV and resultant tunable PL emissions in the range of 390–450 nm which covers most part of the violet–blue window [20–22]. The very narrow emission peaks, high PL quantum yield, high color purity (FWHM being about 12–20 nm), and good chemical/photochemical stability of ZnSe based core/shell structured

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QDs make them attractive choices for the violet QD-LED applications [2,23,24]. By using ZnSe/ZnS QDs as emissive layer, the best reported performance of the QD-LEDs with blue EL emission peak at 441 nm have reached maximum luminance and current efficiency of 1170 cd/m$^2$ and 0.51 cd/A with the inverted structure which cannot be fully solution-processed [20]. For the use of ZnSe/ZnS core/shell QDs to fabricate violet QD-LEDs with fully solution-processed, the maximum luminance and EQE just reach 25 cd/m$^2$ and 0.65% with emission peak at 410–435 nm [21,22]. The reasons for low efficiency and brightness of violet QD-LEDs are mainly attributable to the following three points: (1) larger potential energy barrier at the interface of violet–blue quantum dots and hole transport layer, which result in low hole injection efficiency along with poor external quantum efficiency; (2) the lower QYs of violet–blue quantum dots is a relative critical factor; (3) the photometric quantity of luminance, which is determined by the relative sensitivity of human vision to different wavelengths, shows a much lower luminous efficacy for violet light versus green and red counterparts. Therefore, under the premise of high quality violet QDs, how to select appropriate hole and electron injection materials is the key to fabricate efficient and bright violet QD-LEDs. Recently, the excellent performance of QD-LEDs has been obtained by using metal oxide nanocrystals (especially ZnO) as electron transport [12,15,16]. With regard to hole injection, $WO_3$ and NiO have been used as hole injection/transport layers in QD-LEDs, which promote the hole injection due to the lower hightest occupied molecular orbital (HOMO, from 5.5 to 6.3 eV) [25–27]. For example, Yang et al. reported $WO_3$ nanoparticle-based QD-LEDs with maximum luminance, EQE and peak of current efficiency of 30,600 cd/m$^2$, 3.32% and 10.75 cd/A [27]. However, the performance of devices is still poorer, compared with the organic hole transport materials-based QD-LEDs. Therefore, blending of different organic hole transport materials has been widely used as HTLs in QD-LEDs. Since 2003, Kim et al. [28] have reported that performance of phosphorescent organic light-emitting diodes (PHOLEDs) has been improved by using the mixture of N,N′-di(1-naphthyl)-N,N′-diphenylbenzidine (NPB) and 4,4′,4″-tris(N-carbazolyl)triphenylamine (TCTA) as HTLs. In 2013, Ho et al. [29] demonstrated that the maximum current efficiency of QD-LEDs improved 27% upon 20 wt.% of TCTA adding into PVK due to the more suitable injection barrier of the mixed hole transport layer.

According to our work has been reported [30], herein, we detailedly demonstrate bright, efficient, and heavy-metal-free ZnSe based QD-LEDs by choosing suitable hole transport layers, which cater to the direct carrier injection into QDs and the efficient radiative exciton recombination within QDs. The performance of QD-LEDs was investigated with different hole transport layers (HTL) including poly(4-butyl-phenyl-diphenyl-amine) (poly-TPD), poly[9,9-dioctylfluorene-co-N-[4-(3-methylpropyl)]-diphenylamine] (TFB), and poly-N-vinylcarbazole (PVK). The results show that when TFB is used as hole transport layer, low turn-on voltages and high brightness violet QD-LEDs can be obtained, but with low external quantum efficiency. And when PVK is used as hole transport material, highly efficient violet QD-LEDs can be fabricated but with lower maximum luminance and higher turn-on voltages compared with counterpart using TFB. However, the turn-on voltage, brightness and efficiency can all benefit from the using of TFB and PVK mixture in a certain proportion as HTL. The resulting QD-LEDs record 7.39% of EQE and 2856 cd/m$^2$ of maximum brightness with narrow FWHM less than 21 nm. Such high value of the peak EQE is 4 times more than the best performance of Cd-based violet QD-LEDs. These results represent significant improvements in the performance of heavy-metal-free violet QD-LEDs in terms of efficiency, brightness, and color purity, and also offer a practicable scheme for the realization of heavy-metal-free QD-based violet lighting applications.

## 2. Experimental section

### 2.1. Chemicals

All reagents were used as received without further experimental purification. Zinc oxide (ZnO, 99.99% powder), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), 1-octanethiol (OT, 98%), zinc acetate (99.99%), dimethyl sulphoxide (DMSO, 99.7%), tetramethylammonium hydroxide (TMAH, 97%), and selenium (Se, 99.99%, powder) were purchased from Aldrich. Chlorobenzene (analytical grade), hexanes (analytical grade), paraffin oil (analytical grade), and methanol (analytical grade) were obtained from Beijing Chemical Reagent Ltd., China.

### 2.2. Synthesis of ZnSe core QDs at low temperature and ZnSe/ZnS core/shell QDs under high temperature

ZnSe cores were prepared according to the previous literature of our group [23]. In a typical synthesis, 2 mL Se precursor and 8 mL paraffin oil were heated to 300 °C under nitrogen flow in a 100 mL flask. Next, 1.3 mL Zn precursor solution was injected, and then maintained for 10 min for the formation of ZnSe core QDs. Subsequently the reaction temperature was set at 320 °C without any purification steps, then 2 mL OT mixed with 20 mL of Zn precursor was added at a rate of 6 mL/h for the shell growth process which lasted for 4 h. Aliquots of QDs were taken during the reaction to analyze the development of ZnSe/ZnS core/shell QDs. After the reaction was completed, the temperature was cooled down to room temperature and the QDs were purified using acetone or methanol.

### 2.3. Fabrication and characterization of QD-LEDs

ZnO nanoparticles (NPs) were synthesized by a solution-precipitation process using Zn acetate and tetramethylammonium hydroxide (TMAH) [13]. For a typical synthesis, a solution of zinc acetate in dimethyl sulphoxide (DMSO) (0.5 M) and 30 mL of a solution of TMAH in ethanol (0.55 M) were mixed and stirred for 1 h in ambient air, then washed and dispersed in ethanol at a concentration of ~30 mg/mL. QD-LEDs were fabricated on glass substrates coated with ITO with a sheet resistance of ~20 $\Omega$ sq$^{-1}$. The substrates were cleaned with deionized water, acetone and isopropanol, consecutively, for 15 min each, and then treated for 15 min with ozone generated by ultraviolet light in air. These substrates were spin-coated with PEDOT:PSS (AI 4083) and baked at 150 °C for 15 min in air. The coated substrates were then transferred to a $N_2$-filled glove box for spin-coating of the poly(4-butyl-phenyl-diphenyl-amine) (poly-TPD), poly[9,9-dioctylfluorene-co-N-[4-(3-methylpropyl)]-diphenylamine] (TFB), and poly-N-vinylcarbazole (PVK), ZnSe/ZnS QDs and ZnO nanoparticle layers. The poly-TPD, TFB and PVK hole-transport layer were spin-coated using 1.5 wt.% in chlorobenzene (3000 rpm for 30 s), followed by baking at 150 °C for 30 min. A series of different thickness of TFB and PVK layers can be obtained by controlling the spin speed from 1000 to 4000 rpm (that is 1000, 2000, 3000 and 4000 rpm corresponding to the thickness of ~33, ~29, ~25 and ~22 nm, respectively). This was followed by spin-coating of ZnSe/ZnS QDs (15 mg/mL, in toluene) and ZnO nanoparticles (30 mg/mL, in ethanol) layers followed by baking at 145 °C for 30 min. The spin speed is 2000 rpm for the QD layer and 3000 rpm for the ZnO nanoparticle layer to achieve layer thickness of ~25 and ~30 nm, respectively. These multilayer samples were