



High-performance azure blue quantum dot light-emitting diodes via doping PVK in emitting layer



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ABSTRACT

Highly bright and efficient azure blue quantum dot-based light-emitting diodes (QD-LEDs) have been demonstrated by employing ZnCdSe core/multishell QDs as emitters and the crucial development we report here is the ability to dramatically enhance the efficiency and brightness through doping poly vinyl(*N*-carbazole) (PVK) in the emissive layer to balance the charge injection. The best device displays remarkable features like maximum luminance of 13,800 cd/m², luminous efficiency of 6.41 cd/A, and external quantum efficiency (EQE) of 8.76%, without detectable red-shift and broadening in electroluminescence (EL) spectra with increasing voltage as well as good spectral matching between photoluminescence (PL) and EL. Such azure blue quantum-dot LEDs show a 140% increase in external quantum efficiency compared with QD-LEDs without PVK. More important, the peak efficiency of the QD-LEDs with PVK dopant is achieved at luminance of about 1000 cd/m², and high efficiency (EQE > 8%) can be maintained with brightness ranging from 200 to 2400 cd/m². There are two main aspects of the role of PVK in the proposed system. Firstly, the lower HOMO of PVK than (poly[9,9-dioctylfluorene-co-*N*-[4-(3-methylpropyl)]-diphenylamine] (TFB) can reduce the potential barrier for 0.4 eV at the interface of QDs and hole transport layer which could result in higher hole injection efficiency along with good EQE as compared to TFB-only HTLs. Secondly, with PVK acting as buffer layer of TFB and QDs, the exciton energy transfer from the organic host to the QDs can be effectively improved.

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1. Introduction

Inorganic semiconductor quantum dots (QDs) show great superiority over organic, polymeric or metal-organic emitters in easily tunable emissions via particle-size control, incomparable color purity, extraordinary thermo- and photo-stability and inertness concerning humidity and oxygen [1–5]. So the colloidal QDs have been proposed as ideal emitter candidates for the development of solution-processable thin film light emitting diodes (LEDs). Since the first QD-LEDs were demonstrated, the device performance has been improved rapidly [6–15]. For examples, the maximum luminance for red emitting QD-LEDs has reached up to

40,000 cd/m² with external quantum efficiency (EQE) of 20.5% [10]; and for green QD-LEDs, Kwak et al. [11] and Yang [12] demonstrated green-emitting QD-LEDs with maximum brightness of 218,800 cd/m² and highest EQE of 14.5%, respectively. Recently, we demonstrated deep blue-emitting (420–455 nm) QD-LEDs with a record EQE as high as 12.2% with relatively luminance about 8000 cd/m² [13], and blue (468 nm) QD-LEDs with the highest luminance values (4700 cd/m²) by using Zn_{1-x}Cd_xS_{1-y}Se_y/ZnS core/shell QDs as emitters [16]. Obviously, the luminance of blue QD-LEDs is still not quite on a par with either their green, red, even deep blue counterparts. This may act as the major limiting factor for the fabrication of high quality full-color quantum dot displays. The development of highly bright, efficient and low-cost azure blue (470–485 nm) QD-LEDs will further promote applications such as solid-state lighting and next-generation displays. The luminance for current blue QD-LEDs is still relatively low, even though blue is one of the tri-primary colors. The reasons can be concluded as large potential energy barrier at the interface of blue quantum dots and

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hole transport layer (HTL), low quantum yields (QYs) of blue quantum dots, and small numeric values for blue spectral range in luminosity function. Early efforts for the fabrication of highly bright and efficient blue QD-LEDs have mainly been devoted to minimize interlayer potential energy barriers and thus enhancing the injection efficiency of carriers [14–20]. Although the efficiency of blue QD-LEDs has been improved a lot, their brightness still remains relatively low [13,14]. Another factor that can be used to improve the luminance and efficiency of blue QD-LEDs is the Förster resonance energy transfer (FRET) process [19,20], in which exciton energy formed in the organic host can be transferred to the quantum dots by means of dipole–dipole interaction due to their comparable bandgaps. The long-chain fatty acids are usually being used as capping ligands for QDs, which are sandwiched between carrier transport layers in QD-LEDs [8,21]. The operating mechanism of such devices is based mainly on the balanced injection of carriers and efficient energy transfer from transport layers to QDs. Owing to the long chain capping ligands, these devices may suffer from imbalanced charge injection and inefficient energy transfer [22]. Thus, optimizing the surface capping ligands of QD emitters with suitable short-chain ones would be an effective way to approach more balanced charge injection and efficient FRET, and then help to fabricate highly bright and efficient QD-LEDs spanning the whole spectral region of blue [13].

Here, the crucial development we report is the ability to dramatically enhance the efficiency and luminance by doping small amount of poly vinyl(N-carbazole) (PVK) in the emissive QD layer on the basis of reduction of distance among the ZnCdSe core/multishell QDs to achieve a well-balanced charge injection. By fabricating devices with QDs capped with short-chain 1-octanethiol (OT) molecules, our best device displays maximum luminance of 13,700 cd/m², luminous efficiency of 4.56 cd/A, and EQE of 6.27%. The introduction of PVK dopant in QD layer can effectively approach balanced injection of carriers, which lead to the significant performance improvement with maximum brightness of 13,800 cd/m², high EQE of 8.76%, and peak luminous efficiency of 6.41 cd/A. No red-shift or broadening in electroluminescence (EL) spectra with increasing voltage were observed, while good spectral matching between photoluminescence (PL) and EL was maintained. This is the first demonstration of blue QD-LEDs with brightness higher than 10,000 cd/m² and records the highest efficiency for azure blue (470–485 nm). More importantly, the peak efficiencies of the QD-LEDs with PVK-doped emitter are achieved at about 1000 cd/m², and high efficiencies (EQE > 8%) are maintained in the brightness range of 200–2400 cd/m². These characteristics are highly desirable for practical applications such as displays and lighting.

2. Experimental section

2.1. Synthesis of ZnCdSe/ZnSe/ZnSeS/ZnS core/multishell QDs with azure blue emission

The synthesis of ZnCdSe core and ZnCdSe/ZnSe/ZnSeS/ZnS core/multishell QDs for azure blue emission was similar to our previously reported method with some modification on the growth of shell materials (see [Supporting Information](#)).

2.2. Fabrication and characterization of QD-LEDs

ZnO nanoparticles (NPs) were synthesized according to previous report [12,23]. QDs were dispersed in toluene contains certain amount of PVK. Specifically, PVK were first dissolved in toluene under sonication with concentrations of 0.2–1.2 mg/mL, then QDs were added to obtain QD solution of 15 mg/mL. QD-LEDs were

fabricated on glass substrates coated with ITO with a sheet resistance of $\sim 20 \Omega \text{ sq}^{-1}$. 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 N₂-filled glove box for spin-coating of the (poly[9,9-dioctylfluorene-co-N-[4-(3-methylpropyl)]-diphenylamine] (TFB), ZnCdSe/ZnSe/ZnSeS/ZnS core/multishell QDs and ZnO NP layers. The TFB layer were spin-coated using 1.5 wt% in chlorobenzene (2000 rpm for 30 s), followed by baking at 120 °C for 30 min. This was followed by spin-coating of ZnCdSe/ZnSe/ZnSeS/ZnS core/multishell QDs (15 mg/mL) and ZnO NPs (30 mg/mL, in ethanol) layers followed by baking at 75 °C for 30 min. The spin speed is 1500 rpm for the QD layer and 3000 rpm for the ZnO nanoparticle layer to achieve layer thickness of ~ 25 nm and ~ 30 nm, respectively. These multilayer samples were then loaded into a custom high-vacuum deposition chamber (background pressure, $\sim 8 \times 10^{-7}$ torr) to deposit the top Al cathode (100 nm thick) patterned by an in situ shadow mask to form an active device area of 4 mm².

2.3. Characterization

Room temperature UV–vis absorption and PL spectra were measured with an Ocean Optics spectrophotometer (mode PC2000-ISA). PL quantum yields (QYs) were collected using an absolute PL QYs measurement system (FLSP920) in an integrating sphere. Transmission electron microscopy (TEM) studies were performed using a JEOL JEM-2010 electron microscope operating at 200 kV. Current–luminance–voltage characteristics were measured using an Agilent 4155C semiconductor parameter analyser with a calibrated Newport silicon diode. The luminance was calibrated using a Minolta luminance meter (LS-100). The electroluminescence spectra were obtained with an Ocean Optics spectrometer (USB2000) and a Keithley 2400 source meter.

3. Results and discussion

Ternary CdZnSe QDs have received great attention not only because they have tunable emissions determined by the composition across the blue–green spectrum range but also their high PL QYs and stability [24,25]. The blue emitting alloyed CdZnSe QDs showed higher PL QYs than blue emitting CdSe [24]. Moreover, the alloyed QDs have shown interesting properties that are not observed in the binary QD systems such as the core/shell CdZnSe/ZnSe QDs showed unusual nonblinking behavior in contrast to CdSe-based QDs whose PL turns on and off intermittently [26]. Nonblinking alloyed QDs would be very useful in applications that require a continuous output of photons such as light emitting diodes, photoelectrodes or biolabeling [27]. This is one important reason for our choice of ZnCdSe/ZnSe/ZnSeS/ZnS core/multishell QDs as emitter. The ZnCdSe core with diameter of 3.5 nm (Fig. S1) and PL peak of 471 nm (Fig. S2a) were prepared according to our previously reported method but with modified growth of ZnSe/ZnSeS/ZnS shells. The overcoating of ZnSe/ZnSeS/ZnS shell adopted high temperature (310 °C) instead of conventional low temperature shell growth for ZnSe and ZnS (240–260 °C), and the shelling process lasted up to several hours. This is much different from conventional growth of core/shells QDs. High growth temperature and long growth time can help to form ZnCdSeS/ZnSeS alloyed layer, which can afford a smooth confinement potential at core/shell interface and minimize Auger recombination (AR). This process can improve not only the PL QYs but also the stability of QDs. Fig. 1a shows the UV–vis and PL characteristics of ZnCdSe/ZnSe/

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