Efficient quantum dot light emitting diodes for solid state lighting and displays

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**EFFICIENT QUANTUM DOT LIGHT EMITTING
DIODES FOR SOLID STATE LIGHTING AND
DISPLAYS**

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Abstract

Quantum dot (QDs) based light emitting diodes (QLEDs) have received considerable attention as candidates for the next generation lighting and display systems owing to their narrow emission linewidth, high brightness, colour tunability, and cost-effective fabrication techniques. Despite the significant advances in QLED field recently, there are still multiple drawbacks hindering the ultimate research-to-market transformation of the QLED technology. The focus of this study is to address some of these challenging problems of QLEDs including the efficiency, stability, toxicity and flexibility, and to develop more efficient QLEDs that generate high-quality lighting.

The efficiency of QLEDs was dramatically improved by our enhanced light out-coupling mechanism. A layer of large-scale, periodic zinc oxide (ZnO) nanopillar arrays was grown on the glass substrate by a simple and efficient non-wetting templates (PRINT) method. With the layer of ZnO nanopillars as an optical out-coupling medium, a record current efficiency (CE) of 26.6 cd/A was achieved. Meanwhile, the corresponding external quantum efficiency (EQE) of 9.34% is the highest EQE value ever reported for green QLEDs. This is the first study offering detailed insights into the light extraction efficiency enhancement in QLED devices.

In order to improve QLEDs' stability, an efficient QLED using an inorganic tungsten oxide (WO₃) nanoparticle (NP) film as hole injection layer (HIL) was fabricated. The fully functional WO₃ interfacial layers deposited from WO₃ NPs dispersions could be obtained by low temperature annealing and the resulting WO₃ NP-based QLEDs exhibited a superior device performance

compared to that of the polyethylene dioxythiophene: polystyrene sulfonate (PEDOT:PSS)-based QLEDs. Meanwhile, these WO₃ NP-based devices showed an obvious improvement in the device stability and the operating lifetime was increased by approximately two-folds. Furthermore, by utilizing WO₃ and ZnO NPs as the hole and electron transport layers, respectively, an all solution-processed QLED with double-sided metal-oxide (MO) nanoparticle charge transport layers (CTLs) was fabricated. The operating lifetime for the resulting MO NP-based QLEDs was about 20 times longer than that of the PEDOT:PSS-based QLEDs.

The cadmium (Cd)-free QLEDs were also studied to address the toxicity problem. Firstly, a controlled synthesis of high-quality InP/ZnS core-shell QDs with luminescence tunable over the entire visible spectrum was achieved by a facile one-pot solvothermal method. The Cd-free nanocrystals exhibited excellent optical properties including high quantum yields and good photostability in addition to wide emission spectrum tunability. The photoluminescence full width at half maximum (FWHM) of these InP/ZnS QDs could be as narrow as 38 nm, which is the narrowest linewidth reported for InP-based QDs. Making use of these QDs, we fabricated a white QLED with a high colour rendering index (CRI) of 91. Furthermore, a ternary complementary white QLED with an excellent CRI of 95 consisting of blue component (poly-TPD), green component (QDs) and red component (exciplex formed at the interface between poly-TPD and TPBi) was also demonstrated.

In addition, the flexibility of QLEDs was demonstrated in our highly efficient, large-area QLED tapes emitting in red, green and blue (RGB) colours with top-emitting architecture design. The polyimide tapes were used as

flexible substrates and metallic thin films (Al, Ag) as the electrodes. The brightness and EQE are 20,000 cd/m² and 4.03%, respectively, the highest values reported for flexible QLEDs. Meanwhile, these QLED films are highly flexible and mechanically robust to use as electrically driven light emitting stickers by placing on or removing from any curved surface, possibly facilitating versatile LED applications.

In this thesis, multiple challenging problems of QLEDs were addressed with reasonably good solutions. Light out-coupling strategy enhanced device efficiency, the substitution of organic charge transport materials with MO NP layers improved the stability of QLEDs, the development of high-quality InP-based QDs avoided the toxicity problems of QDs, and the use of Kapton tape and metal electrodes made a significant breakthrough in flexible QLED performance. Our study reported in this thesis contributed to the development and advancement of the QLEDs.

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List of Abbreviations

AFM	Atomic force microscopy
Alq ₃	Tris-8-hydroxyquinoline aluminum
CBP	4,4'-N,N'-dicarbazole-biphenyl
CdO	Cadmium oxide
Cd(OA) ₂	Cadmium oleate
CdSe	Cadmium selenide
CRI	Colour rendering index
DDT	1-dodecanethiol
DI-Water	Deionized water
DMSO	Dimethyl sulfoxide
EBL	Electron-blocking layer
EDS	Energy-dispersive X-ray spectroscopy
EIL	Electron injection layer
EL	Electroluminescence
EQE	External quantum efficiency
ETL	Electron transport layer
FE-SEM	Field emission scanning electron microscopy
FWHM	Full width at half maximum
HIL	Hole injection layer
HOMO	Highest occupied molecular orbital
HTL	Hole transport layer
In(MA) ₃	Indium myristate
InP	Indium phosphide
IQE	Internal quantum efficiency
ITO	Indium tin oxide
LED	Light emitting diode
LEE	Light extraction efficiency
LiF	Lithium fluoride
LUMO	Lowest unoccupied molecular orbital
MoO ₃	Molybdenum oxide
NCs	Nanocrystals
NPs	Nanoparticles
OA	Oleic acid
ODE	1-octadecene
OLED	Organic light emitting diode
PEDOT:PSS	Poly(3,4- ethylenedioxythiophene): poly(styrenesulfonate)
PET	Poly(ethylene-terephthalate)

PL	Photoluminescence
Poly-TPD	poly(N,N'-bis (4-butylphenyl)-N,N'-bis(phenyl)benzidine)
PPV	Poly(p-phenylenevinylene)
P(TMS) ₃	Tris(trimethylsilyl)phosphine
QDs	Quantum dots
QLED	Quantum dot light emitting diode
QY	Quantum yield
RMS	Surface roughness
r.p.m.	Revolutions per minute
SEM	Scanning electron microscopy
SSL	Solid state lighting
TCTA	2,2',2''-tris-(N-carbazolyl)-triphenylamine
TEM	Transmission electron microscopy
TMAH	Tetramethylammonium hydroxide
TOP	Tri-n-octylphosphine
TPBi	2, 2', 2''- (1, 3, 5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)
TPD	N,N'-bis (4-butylphenyl)-N,N'-bis(phenyl)benzidine
UPS	Ultraviolet photoelectron spectroscopy
UV-Vis	Ultraviolet-visible
V ₂ O ₅	Vanadium oxide
V _T	Turn-on voltage. The V _T is defined as the voltage at which the luminance is 1 cd m ⁻² .
WO ₃	Tungsten trioxide
Zn(Acet) ₂	Zinc acetate
ZnDDTC	Zinc diethyldithiocarbamate
ZnO	Zinc oxide
Zn(OA) ₂	Zinc oleate
ZnS	Zinc sulphide
ZnSe	Zinc selenide
Zn-St ₂	Zinc stearate

Chapter 1 Introduction

1.1 Motivation

Today, it is predicted that about 20% of the world's yearly electricity consumed is for lighting, which accounts for nearly 6% of global CO₂ gas emission [1]. Solid state lighting (SSL) based on light emitting diodes (LEDs) such as GaN LEDs and OLEDs, with the internal efficiency near the theoretical limit for the conversion of electrical power into light, have demonstrated in the past few years that LEDs present a huge potential to exceed the energy efficiency of non-LED lighting and displays [2-4]. According to the prediction of US Department of Energy in 2011, if all the traditional lighting sources could be replaced by LED lighting, a 50 % reduction in the lighting-related energy consumption would be achieved by 2025 [5].

Colloidal quantum dot-based light emitting diodes (QD-LEDs or QLEDs in short) as an emerging LED technology shows a highly promising light-source for the next generation lighting and display systems thanks to their narrow emission linewidth [6-8], tunable colour emission spectral window across the visible-near-infrared range [9-11], and cost-effective fabrication techniques [12-14]. Since the first report of QLEDs utilizing CdSe colloidal quantum dots in 1994 [16], QLEDs have received considerable attention for academic research and potential commercialization [17, 18]. After about two decades of research and development, the full-colour and saturated electroluminescence (EL) spectra from the high-performance QLEDs have been achieved (Figure 1-1). Now, QLEDs are emerging as an undeniable competitor to organic light emitting diodes (OLEDs) for lighting and display applications.

Figure 1-1. (a) Photographs of full-colour QLEDs and their corresponding EL spectra. (b) Photograph of a white QLED fabricated by mixing red, green, and blue QDs. (c) Side-by-side QD deposition of red, green, and blue pixels by microcontact printing [18].

1.1.1 Evolution of QLEDs

The first electrically driven QLED was reported by Colvin *et al.* in 1994 [16]. In the initial QLEDs with the structure of ITO/poly(p-phenylenevinylene) (PPV)/CdSe QDs/Mg, the CdSe QDs were used as both the emissive layer and electron transport layer (ETL), and the poly(p-phenylenevinylene) (PPV) served as the hole transport layer (HTL). The EL spectrum of the resulting QLED devices was dominated by the CdSe QD emission, with the tunable emission colour from yellow to red. However, the luminance ($\sim 100 \text{ cd m}^{-2}$) and external quantum efficiency (EQE) (0.001–0.01%) were fairly low due to the low emission efficiency of QDs and imbalanced carrier injection into the QDs. Besides, the combined light emission from other organic charge transport layers in the EL spectra of these QLEDs was often observed, which negatively affects the colour purity. Since then, substantial efforts have been done to optimize the

structure of QLEDs and improve the quality of QDs. In 1998, Mattoussi *et al.* reported pure EL emission from QLEDs by passivating the surface defects of CdSe QDs with organic groups or ZnS, where the EL emission was dominated by QD emission and only very weak EL signal from PPV could be observed at high applied voltages [19]. In 2002, the performance of QLEDs was significantly improved by Coe-Sullivan *et al.* by using single monolayer of QDs formed by a phase separation technique. In their work, the N, N'-bis(4-butylphenyl)-N, N'-bis(phenyl)benzidine (TPD) organic small molecules and tris(8-hydroxyquinoline) aluminum (Alq₃) were used as HTL and ETL, respectively, which facilitated charge carrier injection into QDs. Due to the improved injection of carriers in the QD monolayer, the maximum EQE and luminance for the resulting QLEDs reached 0.52% and 2000 cd m⁻², respectively, which was a dramatic improvement over previously reported QLEDs [20]. For the operating mechanisms of QLEDs, Bulović group made a great contribution, who found excitons formed in the luminescent polymer nearby QD layer could be nonradiatively transferred to QDs, which was essential in designing more efficient QLED devices. Using microcontact printing technique, they further demonstrated a series of QLEDs with widely tunable emission across the entire visible spectrum, with a maximum EQE of 2.7% for orange emitting QLED. To reduce the cost of QLED fabrication, Qian *et al.* demonstrated solution-processed QLEDs with a multilayer structure of ITO/ Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS)/ poly(N,N'-bis (4-butylphenyl)-N,N'-bis(phenyl)benzidine) (poly-TPD)/QDs/ZnO nanoparticles/Al, in which all layers were sequentially deposited on ITO by spin-coating except Al electrode deposited using thermal

evaporation [12]. In 2011, Samsung reported a 4-inch full-colour active matrix QLED display with a resolution of 320×240 pixels [21]. The different coloured QDs were patterned into pixels through a solvent-free transfer printing method, which allowed QLEDs to produce uniform and multi-colour emission. The important breakthrough in improving performance of QLEDs is associated with the recent works of the Lee group [22] and QD Vision [6], who realized a record brightness of 218,800 cd m⁻² and an EQE of up to 18% in QLEDs, respectively, which demonstrated that QLEDs have the capability to compete with other emerging display and lighting technologies.

1.1.2 Why QLEDs?

- ***Saturated colours and tunable emission spectrum***

Colloidal QDs, also known as semiconductor nanocrystals (NCs), have attracted great interest due to their promising applications including light emitting diodes (LEDs) [23-25], lasers [26-28], biomedical imaging [29, 30], and sensors [31]. Currently, CdSe-based QDs have been well developed as the workhorse for these uses [17]. QDs, typically less than 10 nm in diameter, exhibit strongly size-dependent optical and electrical properties due to quantum size effects. The emission colours of QDs can be widely tuned simply changing the QD size (Figure 1-2a). Meanwhile, the linewidth emission from QDs is quite narrow with a full width at half maximum (FWHM) of 20 - 35 nm for CdSe based-QD solutions, which is significantly less than that of organic emitters (typically greater than 50 nm) (Figure 1-2c). Currently, the efficiency for QDs is quite high, a near 100% quantum yield (the ratio of emitted photons and the absorbed photons) has been achieved by growing epitaxial

heterostructures with core-shell morphology which passivates surface non-radiative recombination sites of QDs (Figure 1-2d).

Figure 1-2. (a) Size-dependent colour emissions of core-shell CdSe/ZnS QDs [32, 33]. (b) Low-magnification TEM image of the monodisperse CdSe QDs [34]. (c) Comparison of EL spectra for QLEDs and OLEDs with blue, green, and red emissions [35]. (d) Core-shell structure required to ensure the quality of QDs [33, 36].

- **High brightness**

The significant improvement in brightness of QLED has been achieved, especially for green QLEDs with an inverted structure which has reached 218,800 cd m⁻². Table 1-1 compares the typical luminance of TVs or PC

displays, III-V semiconductor based-LEDs, OLEDs and QLEDs, which demonstrates the competitiveness of QLEDs with other display and solid-state lighting technologies [33]. It can be noted that the difference in the relative sensitivity at different wavelengths for human eyes have to be considered in the practical applications of QLED devices. The relative sensitivity varies significantly across the visible spectral range from 400 to 700 nm, and the human eye reaches its maximum sensitivity at the emission wavelength of 555 nm. Therefore, this is an important reason explaining why the reported brightness for other coloured QLEDs such as blue and red QLEDs is relatively lower than that of green-emitting QLEDs.

Table 1-1. Typical luminance values for displays, III-V semiconductor-based LEDs, OLEDs and QLEDs [33].

Device	Luminance (cd/m ²)
Computer Display	250–500 (operation)
Computer Display	1000 (max. value)
III–V LED	10^6 – 10^7
Organic LEDs	up to 10^5
QD LEDs	10^5

- ***Low-cost manufacture***

Colloidal QDs with surface organic ligands, synthesized from organometallic precursors, are solution-processable. This greatly facilitates low-cost, large-area, deposition techniques such as spin-coating, and inkjet printing for fabricating QLEDs. Recently, Qian *et al.* demonstrated a high-performance QLED by using an all-solution process (Figure 1-3a) [12]. All of

the multilayer structure except two electrodes, consisting of a conducting polymer (PEDOT:PSS) as the hole injection layer (HIL), a conjugated polymer (poly-TPD) as HTL, a core-shell CdSe-based QD emissive layer and a ZnO nanoparticle film as ETL were entirely deposited using spin-coating from their respective solutions. The resulting all-solution processed QLEDs display excellent level of device performance, with the peak luminance values of 4,200 cd/m^2 , 68,000 cd/m^2 , and 31,000 cd/m^2 for the blue, green and orange-red emission, respectively.

Figure 1-3. (a) Device structure of all solution-processed QLEDs. (b) Normalized EL spectra of blue, green and orange-red emitting QLEDs. Inset: the corresponding images for these QLEDs [12].

- **Stable emitters and device structure**

Compared with organic dyes, the inorganic QDs have higher chemical, thermal, and electrical stability in principle. With the development of the QD synthesis technique, the extremely stable QDs have been achieved by over-coating a thick shell on QD core that sustains a high degree of thermal stability and maintain their luminescence [37]. An impressive work on robust QLEDs was reported by Bulović group where the all-inorganic QLEDs were achieved by using p-type NiO as HTL and n-type ZnO:SnO₂ as ETL [38]. These devices showed pure QD emission and were capable of operating at high current densities exceeding 3.5 A cm⁻² (Figure 1-4), which suggested that the all-inorganic QLEDs are stable to a certain extent. Our recent works also showed that it is possible to replace organic charge transport layers with robust metal oxide charge transport layers for building air-stable QLEDs [39,40]. To improve device stability, we fabricated a high-performance QLED with double-sided metal-oxide (MO) nanoparticle charge transport layers. The operating lifetime for the resulting QLEDs was about 20 times longer than that of the QLEDs with organic charge transport layers.

Figure 1-4. (a) EL spectra of the all-inorganic QLEDs. (b) The external quantum efficiency (EQE) of the resulting device as a function of current density. The inset shows a photograph of the red QLED [38].

1.1.3 Structure of QLEDs

A typical structure of QLEDs is outlined in Figure 1-5a. A thin layer of colloidal QDs such as CdSe/ZnS core-shell QDs is sandwiched between HTL and ETL. When the bias is applied, the electrons and holes can be injected into the QD layer from ETL and HTL, respectively. The QLEDs with normal structure have been intensively investigated in the past few years. For example, the high-performance, all-solution processed QLEDs and the highly efficient blue QLEDs have been demonstrated using the normal QLED structure [12,41]. However, recently QLEDs with an inverted structure, comprising a few monolayers of QDs sandwiched between an inorganic metal oxide ETL and an organic HTL, have presented a huge improvement with their record efficiency and brightness (Figure 1-5b) [6,22]. In such inverted QLED structure, the charge injection into QDs is more efficient because of the more matching energy level of ETLs and HTLs to that of QDs. The thickness of the QD emissive layer could be much thicker than that of QD layer in normal QLED structure, more than a few layers of QDs, illustrating the high efficiency of carrier injection in the inverted structure.

Figure 1-5. Device structures of QLEDs: (a) normal structure and (b) inverted structure.

1.1.4 Operating Mechanism of QLEDs

Recent studies revealed that the EL from QLEDs is produced by direct charge injection, Förster resonant energy transfer (FRET), or both (Figure 1-6) [10,17,42]. For the direct charge injection process, electrons and holes are injected from ETLs and HTLs into the QD film when the bias is applied, respectively, whereas a large amount of excitons are formed that subsequently recombine to emit photons. In the case of FRET, the mechanism requires the use of luminescent species such as small molecule organics, polymers or inorganic semiconductors in QLED structure (the luminescent species should be near the QD film). In this process, excitons are first formed on the luminescent species rather than the QD layer, and then the energy of excitons is nonradiatively transferred to QDs via dipole-dipole coupling. The relative contribution for these mechanisms can be varied in the QLEDs with different structures. It has been found that FRET is the dominant QD excitation

mechanism in some QLEDs with double-sided organic small molecule CTLs while inverted QLEDs are more compatible with a charge injection model [17].

Figure 1-6. Energy band diagram of a typical QLED showing the charge injection and energy transfer process [17].

1.1.5 Fabrication of QLEDs

(1) *Synthesis and selection of QDs for QLEDs:* colloidal QDs are a key element for QLEDs and high-quality QDs are necessary for achieving high-efficiency QLEDs [6]. Generally, QDs can be obtained according to a benchmark preparation technique, as shown in Figure 1-7. The organometallic precursor is injected into a hot organic coordinating solvent at temperatures of 150-350 °C, and then the injected precursor decomposes quickly due to the high temperature, followed by a rapid formation of nuclei and growth of tiny crystallites via Ostwald ripening [43,44]. The resulting QDs are easily dissolved in many common solvents such as toluene and chloroform due to the presence of surface organic ligands. In addition, post-synthesis size-selective precipitation is often used to ensure the size uniformity of QDs and increase

dispersity of QDs in solution. The size and emission wavelength of QDs can be precisely tuned by controlling the reaction conditions including reaction temperature, reaction time, and precursor concentration.

Figure 1-7. (a) Schematic illustrating the stages of nucleation and growth for colloidal QDs synthesis according to La Mer model. (b) Experimental setup used for the preparation of colloidal QDs [43].

CdSe-based QDs with core-shell structure are currently the main type of emitters for visible-wavelength emitting QLEDs because of their high efficiency. However, the QDs with different core-shell structures can also affect QLED performance significantly (Figure 1-8). For example, the minimal luminescence quenching in QLEDs can be achieved by using the core-shell QDs with strong confinement potentials resulting in the decreased trap-assisted non-radiative recombination, but at the same time the charge in the electric field accelerates the rate of Auger non-radiative recombination where the energy is

dissipated in the form of kinetic energy to a charge carrier instead of as a photon [45]. However, although the dramatic decrease of the Auger and trap-assisted non-radiative in the QDs with very thick shell due to the reduced electronic confinement, the radiative recombination can be also simultaneously decreased when subjected to an electric field. Therefore, for the selection of QDs used for QLEDs, in addition to the high fluorescence quantum yield, the proper structure of QDs should be also considered.

Figure 1-8. Schematic illustration for the impact of QD structure on the trap-assisted (k_t) and Auger (k_a) nonradiative recombination rate. The “green check” and “red cross” represent positive and negative impact, respectively [45].

(2) **Fabrication techniques for QLED devices:** several major fabrication techniques for current QLEDs are summarized below:

(a) Spin-coating

✧ **Phase separation**

Phase separation is a common spin-coating technique used for preparing ordered, large area QDs monolayers. Figure 1-9 (left panel) shows a typical

phase separation process for QDs and TPD (HTL) [46]. The mixed layer of QDs and TPD is first deposited on the substrate by spin coating a solution of QD and TPD, followed by solvent evaporation. After solvent drying, the QDs rise to the surface of the mixed film, forming the completely separated QD layer and TPD layer. This phase separation process can produce uniform, close-packed, self-assembled QD monolayers on the top of TPD, as shown in Figure 1-9 (right panel). However, the requirement for phase separation is very strict and the resulting QD structure can be affected by a series of preparation conditions and parameters such as QD solution concentration, solvent purity, solvent viscosity, QD size distribution and QD aspect ratio.

Figure 1-9. Schematic depiction of a typical phase separation process for fabricating QLEDs (left panel). AFM images of the QD monolayers on the top of TPD (right panel) [46].

✧ **Layer by layer**

Layer-by-layer spin coating is quite simple and efficient, and has been currently the most popular approach to fabricate QLEDs. Due to the multilayer thin film architecture of QLEDs, the orthogonal solvents are required to avoid

the destruction of the underlying layers when depositing overlayers. For example, in a QLED with a standard structure (ITO/PEDOT:PSS/poly-TPD/QDs/TPBi/Al), PEDOT:PSS as a HIL is first deposited from water solution, and poly-TPD as a hole transport material is then spin-coated from chlorobenzene solution, and subsequently the QDs from toluene solution are spin-coated on the poly-TPD film. However, the loss of material during spin-coating process is very serious (ca. 94%–97%), which increases the cost of QLED fabrication. Additionally, spin-coating process cannot make patterned structure and this method requires a rigid, insoluble charge transport layer (CTL) such as poly-TPD as the underlying layers, which has seriously hindered its application in manufacturing sophisticated QLED structures.

(b) Microcontact printing

Although spin-coating technique is relatively simple and facile, the method cannot meet the demand for state-of-the-art displays due to the impossibility of lateral patterning for multi-colour QDs. Microcontact printing, compatible with a variety of colloidal QDs with different sizes and surface ligands, can be used to produce multi-colour and even white QLED devices [21]. For a typical QD printing process (Figure 1-10a), a single coloured QD solution is first spin-coated on donor substrate, followed by a solvent-free ‘inking’ and stamping process, the uniform QD film is transferred to the display substrate. To generate multi-colour emission, different coloured QDs can be printed on the display substrate by the same process, with precision alignment. Figure 1-10b exhibits a fluorescence micrograph of QD stripes emitting in red, green and blue (RGB) colours on glass substrate prepared by contact printing.

Figure 1-10. (a) Schematic process of microcontact printing. (b) The corresponding fluorescence micrograph of the printed RGB stripes of QDs [21].

(c) Inkjet printing

Despite contact printing can fabricate efficient multi-colour QLEDs, the deposition for each coloured QD layer requires a two-step process (which are spin-coating QD solution onto stamp and transfer QDs to the substrate). This leads to a great deal of materials loss in such approach. Compared with contact printing, inkjet printing with the simplicity of QD deposition only in a predefined pattern saves fabrication cost greatly [47]. The used amount for QDs can be in minute quantities according to the drop-on-demand option, and the deposition of QD film in the patterned substrates can reach an order of micrometer registration accuracy [48]. Using the inkjet printing technique, the full-colour photoluminescence emission from inkjet printed QDs excited via an

AC driven phosphor layer has been achieved [49]. Recently, Jabbour *et al.* demonstrated the DC driven red (R), green (G), and blue (B) QLED arrays via inkjet printing (Figure 1-11) [50]. Currently, the main limitations in inkjet printing technique used for QLED fabrication include the tradeoff of lower resolution of the resulting features and worse film thickness uniformity.

Figure 1-11. Photographs of the inkjet printed QLED devices emitting at RGB colours under operation [50].

(d) Electrophoretic deposition (EPD)

Recently, Song *et al.* developed an EPD method for the large-area preparation of colloidal QD films [51]. The EPD process is accomplished by applying a voltage between two parallel electrodes that are suspended in the solution of QDs, where the electric field can be established between the two electrodes, which drives the QD deposition onto the electrodes, as depicted in Figure 1-12. One of the main advantages of the EPD is that the colloidal QD solutions can be efficiently used in the fabrication process of QLEDs. For example, the large amount of QD solution spun off the substrate in spin-coating process is typically unrecoverable. In addition, the multiple substrates may be simultaneously coated in the EPD bath, which greatly shortens device fabrication process. Meanwhile, the EPD can realize a slow rate deposition of

QDs by adjusting the applied voltage, which can assemble QDs in a more energetically favorable structure on the surface of the substrate. The EPD shows a bright future to replace spin coating for QLED fabrication.

Figure 1-12. (a) Schematic illustration of the EPD process. (b) AFM image showing the surface morphology of the deposited QD film. (c) AFM height image of the QD film [51].

1.2 Objective

Despite a 90% internal quantum efficiency (IQE) has been realized by using highly efficient QD emitters, the EQE is encountering a bottleneck in QLEDs due to the low light extraction efficiency (LEE). In addition, the stability of the present QLEDs is also a big concern for their practical application in lighting and displays. According to the recent report, the lifetimes of QLEDs are of the order of 100 – 1,000 hours when operated at an initial video brightness of 100 cd m^{-2} , which cannot meet the requirement for display application ($>10,000$ hours) [17]. Therefore, in-depth studies focusing on the stability of QLEDs are of critical importance.

On the other hand, the serious drawback of the present colloidal QLED technology is its dependence on cadmium-based QDs, which have severely hindered the ultimate research transformation and commercialization of the QLED technology [33]. Toward this end, many researchers are working on cadmium-free materials. Recently, the great progress on the fabrication of QLEDs employing heavy metal-free colloidal quantum dots has been reported by Xu's group where the yellow, green, red and even white QLEDs using CuInS₂-ZnS QDs were made [13]. However, the emission linewidth of CuInS₂ is far broader than that of CdSe and InP, resulting in substantially worse color purity. Meanwhile, CuInS₂ NCs emitting in the visible region (500-650 nm) lacks blue emission, which is not suitable for various important applications such as multicolor display and lighting where the full colour mixture of fluorescence is essential. As a result, it is still a great scientific challenge to develop high-performance cadmium-free QLEDs using NCs with photometric performance as good as those of CdSe NCs.

Furthermore, QLEDs, typically using a QD film thickness of less than hundred nanometers, are very thin, making them virtually transparent and flexible, which renders them in principle suitable for integration onto flexible substrates. The development of the highly flexible QLEDs, allowing for excellent optoelectronic performance and mechanical properties, may prove useful for creating flexible display technologies.

To overcome these shortcomings and expand the applications of QLEDs, great efforts need to be made for exploring lower cost, higher efficiency, more stable and environmentally-friendly QLEDs.

1.3 Major Contributions

The major contributions of this thesis can be divided into three major parts: the first part is the design, structure fabrication and optimization of QLED architecture for improving their performances in terms of device efficiency and stability. The second part is the development of high-quality cadmium-free QDs and their applications in QLEDs. In the third part, to resolve the flexibility problem of QLEDs, we demonstrate a high-performance, flexible QLED platform by the efficient design of top-emitting device architecture. The detailed contributions for this thesis are summarized below.

- ❖ A QLED with enhanced light out-coupling efficiency was achieved through applying a layer of large-scale, periodic ZnO nanopillar arrays grown on the glass surface of substrate by a simple and efficient non-wetting templates (PRINT) method. With the layer of ZnO nanopillar arrays as optical out-coupling medium, a record current efficiency (CE) of 26.6 cd/A is achieved. Meanwhile, the corresponding EQE of 9.34% is the highest EQE value for green QLEDs. For improving device stability, a stable and highly efficient QLED using an inorganic tungsten oxide (WO₃) nanoparticle (NP) film serving as the HIL has been fabricated. Compared with the present PEDOT:PSS-based QLEDs, the resulting WO₃ NP-based QLEDs exhibit a superior device performance. Furthermore, an all solution-processed QLED with double-sided metal-oxide (MO) nanoparticle CTLs is also achieved by utilizing the WO₃ and ZnO NPs as the HTL and ETL, respectively. In addition to the excellent electroluminescence performance, these devices exhibit a

significant improvement in the device stability and the operating lifetime can be almost 20-fold higher than that of the standard device.

- ❖ A controlled synthesis of high-quality InP/ZnS core-shell QDs with luminescence tunable over the entire visible spectrum was achieved by a facile one-pot solvothermal method. The cadmium-free nanocrystals exhibit excellent optical properties including high quantum yields and good photostability in addition to wide emission spectrum tunability. The photoluminescence FWHM of these InP/ZnS QDs can be as narrow as 38 nm, which is the narrowest linewidth reported for InP-based QDs. Making use of these QDs, we fabricated a white QLED with a high colour rendering index (CRI) of 91. Furthermore, a ternary complementary white QLED with an excellent CRI of 95 consisting of blue component (poly-TPD), green component (QDs) and red component (exciplex formed at the interface between poly-TPD and TPBi) has also been demonstrated.

- ❖ Highly efficient, large-area QLED tapes emitting in red, green and blue (RGB) colours were made with top-emitting design and polyimide tapes serving as flexible substrates. The brightness and EQE are 20,000 cd/m² and 4.03%, respectively, the highest values reported for flexible QLEDs. Meanwhile, these QLED films are highly flexible and mechanically robust to be used as electrically driven light emitting stickers by placing on or removing from essentially any curved surface, facilitating various versatile LED applications.

1.4 Organization

This thesis includes 7 chapters.

Chapter 1 briefs the development of QLEDs and existing problems in the present devices. The evolution of QLED devices and relevant background including the device structure, working principle of QLEDs and fabrication issues are presented, followed by the motivation and the objectives of the thesis, and finally the major contributions of this thesis are discussed.

Chapter 2 demonstrates the substantially enhanced light extraction efficiency in QLEDs by applying a layer of large-scale, periodic zinc oxide nanopillar arrays. The relevant mechanisms on the enhanced light extraction efficiency, which are well consistent with the simulation results are discussed in detail.

Chapter 3 reports a stable and highly efficient QLED using solution-processed WO_3 nanoparticle film as a HIL. The WO_3 interfacial layers deposited from WO_3 NPs dispersions can be fully functionalized via a low annealing temperature. Compared with the present PEDOT:PSS-based QLEDs, the resulting WO_3 NP-based QLEDs exhibit a superior level of device performance. To further improve the device stability, an all solution-processed QLED with double-sided metal-oxide (MO) nanoparticle CTLs has been also demonstrated, in which the WO_3 and ZnO NPs serve as the HTL and ETL, respectively. With the use of inorganic metal oxide nanoparticles, these devices exhibit a significant improvement in the device stability.

The high-quality InP/ZnS core-shell nanocrystals with luminescence tunable over the entire visible spectrum for QLED applications are presented in Chapter 4. These cadmium-free nanocrystals exhibit high quantum yields, wide

emission spectrum tunability and excellent photostability. The FWHM can be as narrow as 38 nm, which is close to that of CdSe nanocrystals. Using the resulting QDs, an InP QDs-based white QLED with a high CRI of 91 is demonstrated.

In Chapter 5, a ternary complementary white QLED with an excellent CRI of 95 consisting of blue component (poly-TPD), green component (QDs) and red component (exciplex formed at the interface between poly-TPD and TPBi) is described. The successful realization of the ternary complementary white QLEDs may provide a promising strategy for design and fabrication of high-performance light sources with multi-colour components.

Chapter 6 develops highly efficient, large-area QLED tapes emitting in red, green and blue (RGB) colours with top-emitting design and polyimide tapes as the flexible substrates. In addition to excellent electroluminescence performance, these QLED films are highly flexible and mechanically robust to use as electrically driven light emitting stickers. They can be placed on or removed from essentially any curved surface, facilitating versatile LED applications. These QLED tapes present a step toward practical quantum dot based platforms for high performance flexible displays and solid-state lighting.

Chapter 7 summarizes the conclusions of the thesis and the future works are also elaborated in detail.

Chapter 2 Low-cost, Large-scale, Ordered ZnO Nanopillar Arrays for Light Extraction Efficiency Enhancement in Quantum Dot Light Emitting Diodes

2.1 *Introduction*

Colloidal quantum dots (QDs) offer the advantageous features of high quantum yield [52-55], narrow emission linewidth [56-59], tunable emission wavelength [9,60-62], and low-cost solution-processed preparation techniques [63-65], which make QDs one of the most promising materials for use in lighting-emitting diodes (LEDs). Recently, electrically driven quantum dot light emitting diodes (QLEDs) have been intensively investigated as candidates for next-generation lighting and displays. QLEDs are competing with state-of-the-art organic light emitting diodes (OLEDs), solid-state lighting and other emerging display technologies [6,17,21,66-69]. However, even though a 90% internal quantum efficiency (IQE) has been realized by using highly efficient QD emitters [6], the external quantum efficiency (EQE) of QLEDs is encountering a bottleneck due to the low light extraction efficiency (LEE) [17]. The EQE of QLEDs depends not only on IQE but also on the external out-coupling efficiency η_{oc} (the ratio of the total number of photons coupled out in the forward direction to the total number of photons generated within the QD emissive layer). For a conventional OLED in a planar waveguide-like structure, most of the generated light (~80%) is lost due to photon trapping in substrate modes, waveguided modes, or photon coupling to surface plasmon modes

associated with metallic electrodes, and finally only around 20% of internally generated photons can be extracted into air [70,71]. Given the structural similarity between QLEDs and OLEDs, it can be expected that the η_{oc} of QLEDs is quite low as well. The low η_{oc} in QLEDs leaves much room for device performance improvement. Meanwhile, the QLED architecture also exists itself speciality. Currently, QLED with an inverted structure, comprising a few monolayers of QDs sandwiched between an inorganic metal oxide electron transport layer (ETL) and an organic hole transport layer (HTL), has risen to prominence due to its record efficiency [6] and brightness [22]. In such an inverted QLED structure, the total internal reflection (TIR) would change to a certain extent because of the large difference in refractive indices between organics ($n \sim 1.75$) [72] and inorganic materials (QDs and inorganic charge transport materials). Moreover, the emission linewidth of QDs is much narrower as compared to many organic dye emitters, which causes the different electroluminescence (EL) intensity enhancement levels by placing a QLED in a resonant microcavity. Therefore, the in-depth studies on the light extraction from QLEDs is essential to improve device performance and understand the underlying device physics.

In this chapter, we report a quantum dot light emitting diode with substantially enhanced light out-coupling efficiency through applying a layer of large-scale, periodic zinc oxide nanopillar arrays. The uniform zinc oxide nanopillar arrays can be obtained by a simple and efficient Pattern Replication In Non-wetting Templates (PRINT) technique. The resulting QLEDs with the ordered zinc oxide nanostructure as light out-coupling medium exhibit superior performance compared to that of the reference QLED. The maximum

luminance, current efficiency (CE) and EQE values are 54,200 cd/m², 26.6 cd A⁻¹ and 9.34%, respectively. To our knowledge, the CE of 26.6 cd A⁻¹ is the record high current efficiency value for QLEDs and the EQE of 9.34% also corresponds to the highest reported EQE value for green QLEDs. The relevant mechanisms on the enhanced light extraction efficiency are discussed in detail, which are well consistent with our simulation results.

2.2 Experiment Section

2.2.1 Synthesis of CdSe/ZnS Core-shell QDs and ZnO NPs

CdSe/ZnS QDs with chemical-composition gradients were prepared according to a method reported in the literature [8]. For a typical preparation of green-emitting QDs, 0.1 mmol of cadmium oxide (CdO), 4 mmol of zinc acetate (Zn(Acet)₂), and 5 mL of oleic acid (OA) were loaded in a 50 mL 3-neck flask, heated to 150 °C under vacuum to form cadmium oleate (Cd(OA)₂) and zinc oleate (Zn(OA)₂). Subsequently, 20 mL of 1-octadecene (1-ODE) was added to the reaction flask, and the reactor was then filled with nitrogen and heated up to 300 °C. At the elevated temperature, 1.6 mL of tri-n-octylphosphine (TOP) with 0.15 mmol of selenium (Se) and 4 mmol of sulphur (S) dissolved was swiftly injected into the flask. After that, the reaction mixture was maintained at 300 °C for 10 min for the QD growth. To purify the synthesized QDs, the reaction mixture was cooled down to room temperature, and the QDs were extracted by the addition of acetone and methanol, followed by centrifugation.

ZnO nanoparticles (NPs) with a typical mean diameter of 3-4 nm were synthesized based on a solution-precipitation process [12]. For a typical

synthesis, zinc acetate in dimethyl sulfoxide (DMSO) (0.1 M, 30 mL) and tetramethylammonium hydroxide (TMAH) in ethanol (0.55M, 30 mL) were fully mixed and stirred for 1 h in ambient air, and then washed at least 4 times with excess precipitant solvents such as hexane:ethanol (1:4 by volume). Finally, the as-prepared white precipitant was dispersed in ethanol at a concentration of $\sim 25 \text{ mg mL}^{-1}$.

2.2.2 Preparation of ZnO Nanopillar Arrays

The large-scale, periodic ZnO nanopillar arrays were prepared on the glass surface of patterned ITO-glass substrate according to a modified pattern replication approach of non-wetting templates (PRINT) technique [73], in which a ZnO thin film of 20 nm is first deposited on glass surface as a ZnO seed layer by RF magnetron sputtering for obtaining high-quality ZnO nanopillar arrays. Next, a polydimethylsiloxane (PDMS) mold was prepared using the patterned silicon master substrate. The PDMS mold was then pressed on the glass surface of substrate that was coated with ZnO precursor solution composed of 0.1 M $\text{Zn}(\text{Ac})_2$ aqueous solution and 0.1 M diethanolamine (DEA) by drop-casting method. The ITO-glass substrate was heated for removing solvent. Subsequently, the mold was peeled off, followed by annealing at 180 °C for 15 min, and the as-prepared ITO-glass substrate with ordered ZnO nanopillar arrays could be obtained.

2.2.3 Device Fabrication

The patterned indium tin oxide (ITO) substrates were thoroughly cleaned by sonication sequentially in nonionic detergent, de-ionized water, acetone, and isopropyl alcohol for 15 min each. The ZnO NP layer was then

spin-coated on the ITO substrate (with ZnO nanopillar arrays on the other side) from ZnO ethanol solution at 1000 r.p.m. for 60 s and annealed at 150 °C for 30 min in a nitrogen glove box. Next, the QD layer was deposited on the ZnO NP layer by spin-coating the QD dispersion (QDs being dispersed in toluene with 15 mg/mL) at a speed of 2000 r.p.m. for 60 s, and cured at 90 °C for 30 min. Subsequently, the 4, 4'-N, N'-dicarbazole-biphenyl (CBP, 60 nm), MoO₃ (10 nm), and Al (190 nm) layers were thermally deposited under a base pressure of $\sim 2 \times 10^{-4}$ Pa. For the deposition of Al electrode, a shade mask was used to define the top Al contact and form an active device area of 9 mm².

2.2.4 Characterization

The electroluminescence (EL) spectra of the QLEDs were measured using a Photo Research PR705 Spectra Scan spectrometer, while the luminance–current–voltage characteristics of the devices were measured simultaneously with a programmable Yokogawa GS610 source meter and a Konica Minolta luminance meter LS-110 in air at room temperature. The integral EL spectra were measured using an integrating optical sphere and the measurement of overall device performance for QLEDs with ZnO nanopillars was carried out using a technique described by Forrest *et al.* [74] in which a pre-calibrated photodiode was placed in contact with the active pixel (the area of photodiode – 1×1 cm² – is much larger than that of the active pixel – 2×2 mm²). The EL emission from QLEDs was first measured as the photodiode current and the driving current of QLED device was also recorded simultaneously. The total device lumiance and efficiency can be calculated by these two quantities together with the integral EL spectra. The photoluminescence (PL) spectra were recorded using a Shimadzu RF-5301PC

spectrofluorophotometer equipped with a 150 W Xenon lamp as the excitation source. The morphologies of the as-prepared ordered ZnO nanopillars were observed using scanning electron microscopy (SEM, JEOL, JSM-5910) and field emission scanning electronic microscopy (FE-SEM, JEOL, JSM-6340F).

2.3 Results and Discussion

2.3.1 Properties of CdSe/ZnS Core-shell QDs

The representative low-magnification transmission electron microscopy (TEM) image of the resulting CdSe/ZnS QDs is shown in Figure 2-1a. We can see that these QDs exhibit a narrow size distribution with an average particle size of ~7 nm. The PL spectrum of the QDs was measured at room temperature (Figure 2-1b). A purely green emission consisting of a band edge emission with a peak wavelength of 504 nm and a linewidth of 30 nm was observed (without surface defect emission). The fluorescence quantum yield (QY) for the purified QDs toluene solution is ~60%. The inset in Figure 2-1b shows an eye-visible photograph of the strong green photoluminescence from the QDs solution excited under UV light.

Figure 2-1. (a) TEM image of the resulting CdSe/ZnS QDs at low magnification. (b) UV-Vis absorption and PL spectra of the resulting CdSe/ZnS QDs. The inset in (b) is the photograph of CdSe/ZnS QDs dispersed in toluene solution.

2.3.2 Electrical Characterization and Optimization

The resulting QLED comprises a multilayer thin film architecture of ITO/ZnO NPs/QDs/4,4'-N,N'-dicarbazole-biphenyl (CBP)/MoO₃/Al, as shown in Figure 2-2a, where MoO₃ was used as the hole injection layer (HIL), CBP as the HTL, CdSe/ZnS QDs were used as the emissive layer (EML), ZnO NP film was spin-casted from ZnO NPs in ethanol solution as ETL, and Al as the anode. Figure 2-2b presents the EL spectrum of our optimized QLED with a 20 nm thick QD layer and a 40 nm thick ZnO NP layer (reference device). The pure green QD emission at a peak wavelength of ~510 nm and a full width at half maximum (FWHM) of 32 nm illustrates the highly efficient recombination of electrons and holes in the QD emissive layer. A corresponding image of the QLED output was recorded at the luminance of 250 cd/m², which displays a uniform, bright and saturated green emission (inset of Figure 2-2b).

Figure 2-2. (a) Schematic of QLED configuration. (b) EL spectrum of the resulting QLED at an applied voltage of 6 V. Inset: the corresponding photograph of the QLED under operation with a pixel size of 3 mm×3 mm.

The typical current density and luminance curves as a function of applied voltage for the device are shown in Figure 2-3a. The maximum luminance reaches 34,900 cd/m² and the turn-on voltage (V_T) of 3 V is relatively low, suggesting a small barrier height for the charge injection into the QDs. The V_T is defined as the voltage at which the luminance is 1 cd m⁻². The current efficiency – external quantum efficiency – current density (CE-EQE-J) characteristics of the QLED exhibit a high device efficiency (Figure 2-3b), with

a maximum CE and EQE of 17.6 cd/A and 6.17 %, respectively, which are the highest reported values for green QLEDs so far [22].

Figure 2-3. (a) Current density-voltage (J-V) and luminance-voltage (L-V) characteristics. (b) Current efficiency and external quantum efficiency versus current density (CE-EQE-J characteristics).

In optimizing the device performance, it is found that, besides the important effects of QD and ZnO NP layer thickness [6,12], the performance of the resulting QLEDs is also strongly dependent on annealing temperature of ZnO NP film. As shown in Figure 2-4a, for the QLED with a 20 nm thick QD layer and a 40 nm thick ZnO NP layer, increasing ZnO annealing temperature from 90 to 180 °C, the V_T of device shows a steady decrease from 4.5 V to 3 V

and the peak luminance of 34,900 cd/m^2 is obtained at the annealing temperature of 150 °C. In Figures 2-4b and 2-4c, it can be observed that the maximum CE and EQE levels of 17.6 cd/A and 6.17 % are also obtained at 150 °C. This is enabled by enhancing the electron transport in ZnO nanoparticle films as increasing annealing temperature so that more charges are injected into QLEDs, which is confirmed by the J-V curves of these devices in Figure 2-4d. Meanwhile, it can be also noted that there is no obvious change in the J-V curves for 150 and 180 °C annealing and for 180 °C annealing the device EL performance becomes even a bit worse, suggesting that 150 °C is the optimal annealing temperature in our study.

Figure 2-4. (a) Luminance-voltage (L-V), (b) current efficiency-current density (CE-J), (c) external quantum efficiency-current density (EQE-J), and (d) current density-voltage (J-V) characteristics for QLEDs with ZnO nanoparticle films annealed at different temperatures from 90 to 180 °C.

2.3.3 Design for Enhancement of Light-outcoupling Efficiency

With the similar structure with OLEDs, the LEE of QLEDs is significantly limited due to reflection from the glass-air interface. It has been previously demonstrated that photonic crystal nanostructure can be used above the glass surface for enhancing the LEE of OLED device where the trapped light within the QLED escapes out into the air due to Bragg diffraction and scattering from the nanostructure on the glass surface [75-80]. For our case, the light extraction enhancement in QLEDs is investigated by attaching the ordered ZnO nanopillar arrays onto the glass surface of ITO-glass substrates, as shown in Figure 2-5a. Our method is quite simple and efficient, and the high-quality ZnO nanostructure can be directly imprinted with precursor solutions according to a modified PRINT technique. Figure 2-5b briefly illustrates the fabrication process for the ZnO nanopillar arrays used here. A polydimethylsiloxane (PDMS) mold was first prepared using the patterned silicon master substrate. The PDMS mold was pressed on the glass surface of patterned ITO substrate that was pre-coated with ZnO precursor solution composed of $\text{Zn}(\text{Ac})_2$, DEA and water in which the sol-gel ZnO nanoparticles were formed. The ITO-glass substrate was then annealed for removing solvent. Subsequently, the mold was peeled off, leaving behind the periodical nanopillar arrays. Finally, the as-prepared substrate was annealed at 180 °C for 15 min. The large-scale ZnO nanopillars were designed with a 200 nm diameter and height and the total thickness for formed ZnO film during the fabrication process of ZnO nanopillar arrays is ~200 nm. Note that prior to the fabrication of ZnO nanostructure a ZnO thin film of 20 nm was first deposited on the glass surface as a ZnO seed

layer by RF magnetron sputtering for obtaining high-quality ZnO nanopillar arrays.

Figure 2-5. (a) Schematic illustration of the QLED with ZnO nanopillar arrays. (b) PRINT process used to fabricate the ordered ZnO nanopillar arrays on the glass surface of ITO-glass substrate.

Figure 2-6 shows the enlarged tilt-view field-emission scanning electron microscopy (FE-SEM) and plane-view scanning electron microscopy (SEM) images for the as-prepared ZnO nanopillar arrays grown on the glass surface of QLED substrate. In Figure 2-6a, it can be clearly observed that the imprinted ZnO nanopillar arrays exhibit uniform size distribution with a nanopillar array pitch of 600 nm. In addition, the enhancement of light out-coupling by the photonic crystals is based on Bragg diffraction and scattering. It is therefore desirable to choose an approximate nanopattern period that is comparable to the wavelength of the light for maximized light out-coupling. In our case, the pitches of ZnO nanopillar arrays can be conveniently and accurately controlled only by adjusting the size of the patterned silicon master substrate. As shown in Figures 2-6b, c and d, the different pitches of the periodic ZnO nanopillar

arrays were obtained and measured by the SEM image to be 400 nm, 600 nm, and 800 nm for our present study, respectively.

Figure 2-6. (a) 60° side view FESEM image of ordered ZnO nanopillar arrays with a pitch of 600 nm. The top view SEM images of the ZnO nanopillar arrays with a pitch of (b) 400 nm, (c) 600 nm, and (d) 800 nm, respectively.

Figure 2-7a shows the EL spectra for the reference device without ZnO nanopillar arrays and devices with ZnO nanopillar arrays measured using an integrating optical sphere at a current density of 100 mA/cm². Comparisons of these integral EL spectra show no significant difference in the EL peak positions (at ~510 nm) for these devices. However, EL intensities obtained from the QLEDs with ZnO nanopillars were obviously enhanced, especially for the device with a ZnO nanopillar array pitch of 600 nm. Figure 2-7b presents the normalized angular emission intensity for these devices. It can be noted that the reference device and device with ZnO pillar array pitch of 400 nm show similar angular distribution characteristics with an approaching Lambertian emission

pattern, which implies that the diffraction effect for the device with 400 nm pitch ZnO pillars is not very significant. The QLEDs with the ZnO pillar array pitches of 600 nm and 800 nm, however, show quite different angular emission behaviours that presents non-Lambertian emission distributions. The emission intensity decreasing for the device with the 600 nm pitch ZnO pillars is much slower and the device with the 800 nm pitch ZnO pillars show its maximum emission intensity at a viewing angle of 30°. The non-Lambertian emission behaviour for the two QLEDs can be explained by the grating effect of the ordered ZnO nanostructure. The trapped light in QLEDs can be extracted into air due to the presence of ZnO nanopillar arrays, and if assuming that incidence angle is 0° the emission intensity of diffracted light can be written as [73]

$$f(\theta) = A \times \left\{ \cos \left[\frac{\pi p}{\lambda} \times \sin(\theta) \right] \right\}^2 \quad (2.1)$$

Where θ presents the emission angle viewed from air, A is the amplitude of light extracted by the grating, p is the pitch of periodic ZnO nanopillar arrays, and λ is the emission wavelength of QLEDs which is set to the peak wavelength 510 nm in our case.

The EL intensity of the diffracted light emitted from the QLEDs with different ZnO array pitches as a function of the emission angle is shown in Figure 2-7c, which is obtained by subtracting the total angular emission for the corresponding QLEDs with that of the reference device. The resulting data are further fitted using Equation (2.1) and the fitted curves show a good agreement with our experimental results. The constant A of light extracted by the ZnO nanopillars, estimated from the fitting curves, is 0.09, 0.286, and 0.2 for QLEDs with a ZnO pillar array pitch of 400 nm, 600 nm, and 800 nm, respectively. It

can be noted that the fitting coefficient for the device with 400 nm pitch ZnO pillars is much smaller, which indicates the weak diffraction grating effect of ZnO nanopillar arrays. The enhanced device performance for these QLEDs with ZnO nanopillar arrays is shown in Figure 2-7d, e and f. In Figure 2-7d, the QLED with 600 nm pitch ZnO pillars exhibits the highest brightness and its luminance reaches 54,200 cd/m^2 at the applied voltage of 11 V, 1.5 folds higher than that of the reference device. Figures 2-7e and 2-7f present the EQE-J and CE-J curves of device. With the incorporation of ZnO nanopillars, the device with the ZnO nanopillar array pitch of 600 nm made a record CE of 26.6 cd/A at a luminance of 29,690 cd/m^2 . This corresponds to an EQE level of 9.34%, significantly higher than that of the reference device (6.17%), which is enhanced by a factor of 51.4%.

Figure 2-7. (a) EL spectra of QLEDs acquired from an integrating optical sphere. (b) Angular dependencies of the reference device and devices with different ZnO array pitches. (c) Fitting of the angular distribution for QLEDs with different ZnO array pitches. (d) Luminance, (e) current efficiency, and (f) EQE versus current density.

2.3.4 Simulation Analysis

The increase in LEE of QLED structure due to the presence of ZnO nanopillar arrays is verified using two-dimensional LUMERICAL FDTD simulation. A 20 μm wide simulation area is constructed to include multiple period of patterning. Physically matched layers are used as boundary condition to surround the simulation area to absorb any light radiation impinging on it. Dipole light source is placed in the QD emissive layer to replicate the light radiation generated due to electron-hole recombination. The ZnO nanopillar arrays with 200 nm height, 200 nm diameter and 600 nm pitch are placed over the 200 nm thick ZnO seed layer. The LEE is measured from 400 nm to 700 nm wavelength in the far-field after integrating all extracted light radiation in 1° solid angle, and the LEE enhancement in QLEDs is obtained by dividing the total power coming out of device with ZnO nanopillar arrays (in air) to the total

power for reference device. As shown in Figure 2-8a, most of the light that is generated in the QD emissive region suffers the total internal reflection from glass-air interface and is trapped within QLED architecture. In contrast, Figure 2-8b shows the light escaping out from QLED due to the presence of ZnO nanopillar arrays on the top of glass surface, which thus significantly enhances the LEE of QLEDs. It can be clearly quantified from the data in Figure 2-8c that the LEE enhancement is ~ 1.5 fold at 510 nm emission wavelength as compared with the reference device, which is in excellent agreement with our experimental findings.

Figure 2-8. FDTD results showing (a) light trapped inside glass due to reflection from glass-air interface and (b) light escaping out due to the presence of periodic ZnO nanopillar arrays on top of glass surface of QLEDs. (c) LEE enhancement in the QLED with ZnO nanopillar array pitch of 600 nm.

A QLED architecture constituting multiple organic and inorganic thin layers with varying indices behaves as an OLED microcavity [81-86], in which the light radiation is partially reflected and transmitted through different multilayers depending on their refractive indices when the photon is emitted from the QD layer. Therefore, the performance of the resulting QLEDs can be also affected by the microcavity structure of device. In QLED microcavity, thick metal electrode at one end of a QLED device serves as one of the reflecting mirrors; whereas, different organic and inorganic multilayers acts as partial reflector at other end. It is worth mentioning that QLED architecture has more distinctive refractive indices compared with OLEDs due to the inorganic QD and ZnO layers generally have higher refractive indices over organic materials. To explore the microcavity effects in the resulting QLEDs, the 2D-QLED structure without the incorporation of ZnO nanopillar arrays is designed in LUMERICAL FDTD graphic user interface (Figure 2-9). The device microcavity structure allows the formation of a standing wave within the cavity. This means that the electric field profile along the length of the microcavity is not constant and has peaks and nodes. The position of QD layer must align with the peak of electric field intensity profile within microcavity structure for obtaining high-performance QLEDs, this indicates the optical density of states should be high over the QD emissive layer. If the position of QD layer lines up with the node of electric field intensity profile, the spontaneous emission from the QD layer is suppressed rather than enhanced. In the designed simulation, the QLED microcavity is illuminated with a plane wave source with wavelength varying from 400 nm to 700 nm. The total electric field inside the microcavity is visualised using a 2D frequency domain field profile monitor. This monitor

helps in imaging the position of cavity modes within the optical microcavity. Similarly, the refractive index of each layer is monitored using refractive index monitor. Periodic boundary conditions are used in y direction as for $10\ \mu\text{m}$ wide FDTD simulation area; whereas, physically matches layer is used at the top and metal boundary condition is used at the bottom. Figure 2-9a shows the 2D-FDTD refractive indices of multi-layered QLED structure and the variation of total electric field (standing wave) within the QLED microcavity. The FDTD simulation results in Figure 2-9b clearly show that the position of the QD emissive layer in our QLED (from $0.24\ \mu\text{m}$ to $0.27\ \mu\text{m}$ on y -axis) quite matches with the peak of total electric field and hence enhances the emission of photons.

Figure 2-9. (a) Refractive indices of different organic and inorganic layers of QLEDs (from the top to the bottom: Glass/ITO/ZnO NPs/QDs/CBP/MoO₃/Al). (b) Total electric field at 510 nm wavelength with in the QLED microcavity simulated using LUMERICAL FDTD Solutions.

In addition, it is found that the cavity mode can also increase the LEE of green emitting QLEDs by transmitting particular wavelength (green range) while suppressing other wavelengths, which is confirmed by measuring the reflection from the QLED microcavity using the same FDTD simulation. The

1D frequency-domain monitor is positioned behind the plane wave source to measure this reflection. As shown in Figure 2-10, the QLED microcavity suppresses the reflection around 500 nm optical wavelength, and thus gives high transmission for the green wavelength.

Figure 2-10. Reflection and transmission spectra for the QLEDs.

2.4 Conclusion

We have demonstrated, for the first time, the dramatically enhanced light extraction in QLEDs based on a layer of large-scale, periodic ZnO nanopillar arrays fabricated by a simple and efficient PRINT method. The resulting QLED with ZnO nanopillar array pitch of 600 nm showed a record CE of 26.6 cd/A. The maximum EQE of 9.35% achieved in the present work is also the highest EQE value reported for green QLEDs to date, which corresponds to 51.3% efficiency enhancement in total light output compared with the reference device. Two-dimensional Lumerical finite difference time domain (FDTD) simulations reveal that the significant light out-coupling efficiency

improvement is attributed to the effective diffraction of light trapped in the glass mode due to the presence of ZnO nanopillar arrays and the microcavity effects in the inverted QLEDs. These results suggest that the cost-effective ZnO nanopillars are promising light out-coupling layer for improving QLED performance and our method may also have important implications for understanding and designing high-performance QLEDs by enhancing light extraction efficiency.

Chapter 3 Efficient and Stable Quantum Dot Light Emitting Diodes with Metal-Oxide Nanoparticle Charge Transport Layers

3.1 Introduction

Ever since the first demonstration of quantum dot-based light emitting diodes (QLEDs) two decades ago [16], rapid progress has been made in the device performances owing to the technological development and accumulation of relevant knowledge in materials and device architectures, i.e., understanding the underlying device physics [87-89], designing more efficient device architectures [22,90-93], and improving quantum dot properties by adjusting their composition and structure [6,41,94]. Till date, QLEDs have emerged as an undeniable competitor to organic light emitting diodes (OLEDs) for lighting and display applications. However, despite their apparent advantages, long-term stability of QLEDs is still a big concern for their practical applications.

Currently, polyethylene dioxythiophene:polystyrene sulfonate (PEDOT:PSS) is the most widely used buffer layer on an indium tin oxide (ITO) electrode for the fabrication of QLEDs. However, the aqueous PEDOT:PSS dispersion causes a serious side effect on the device stability due to its hygroscopic nature as well as acidic nature corroding the ITO electrode, resulting in the reduction of device lifetime [95,96]. In addition, the organic interfacial buffer layers have inferior thermal stability compared with the inorganic charge transport materials. Efforts to replace PEDOT:PSS with metal-oxides such as tungsten-, molybdenum-, nickel-, copper (I)-, rhenium-, or

vanadium-oxides (i.e., WO_3 , MoO_3 , NiO , Cu_2O , ReO_3 , or V_2O_5) have received considerable attention in the past few years [38, 97-105]. In particular, the efficient hole injection from highly n-doped WO_3 and MoO_3 with remarkably deep lying electronic states into organic materials has been demonstrated [106-109]. However, their unique electronic properties have so far been primarily achieved using thin films made by high-cost thermal evaporation under vacuum, which presents disadvantages due to the cost issues and incompatibility with roll-to-roll scalable manufacturing as well as the possible physical damage introduced into QDs. On the other hand, it has been found that metal-oxide nanoparticles (NPs) as the interfacial buffer layers are often more efficient as compared to their bulk counterparts. For example, ZnO nanoparticle films as the electron transport layers (ETLs) prepared by a sol-gel method have been introduced by Qian *et al.*, resulting in all-solution-processed QLEDs with the peak luminance values of $31,000 \text{ cd m}^{-2}$, $68,000 \text{ cd m}^{-2}$ and $4,200 \text{ cd m}^{-2}$ for red, green and blue devices, respectively, which are among the highest reported thus far [12]. Furthermore, Meyer's group recently reported the preparation of MoO_3 nanoparticle films by a facile solution process where the MoO_3 was spin-coated on ITO substrate from a suspension containing MoO_3 nanoparticles and a block copolymer dispersing agent in xylene [110]. However, the resulting films require an extra O_2 -plasma treatment to remove the polymeric dispersing agent for facilitating hole injection into the device and the surface of the resulting MoO_3 nanoparticle film was rough. Therefore, as such, in-depth studies focusing on solution-processed inorganic interfacial buffer layers are of critical importance for improving QLED performance.

In this section, we demonstrate high-performance and stable QLEDs

with solution-processed metal-oxide (MO) NPs as charge transport layer (CTL). Firstly, we fabricated a WO₃ NP-based QLED by using an inorganic WO₃ nanoparticle film as hole injection layer (HIL) to replace organic PEDOT:PSS film. The fully functional WO₃ interfacial layers deposited from WO₃ nanoparticle dispersion in ethanol can be obtained by low annealing temperatures without further O₂-plasma treatment (annealing temperature can be as low as 80 °C). Note that the annealing temperatures are much lower than that of PEDOT:PSS (120-150 °C). In addition to the enhanced device stability, the resulting WO₃ NP-based QLEDs also exhibit superior electroluminescence (EL) performance compared to that of the present PEDOT:PSS-based QLEDs, with a maximum luminance of 30,006 cd/m², an external quantum efficiency (EQE) of 3.32%, and a peak current efficiency (CE) of 9.75 cd A⁻¹. To further improve the stability of QLED devices, we designed an all solution-processed QLED with double-sided metal-oxide (MO) nanoparticle CTLs by using WO₃ and ZnO NPs as the respective hole and electron transport layers, in which all of materials are stable inorganic materials except poly(N,N'-bis (4-butylphenyl)-N,N'-bis(phenyl)benzidine) (poly-TPD). The poly-TPD has the advantages of good chemical resistance to organic solvents used for subsequent QD layer deposition, and widely used as the organic hole transport material [13]. The resulting best device exhibit a high luminance of 21,300 cd m⁻², a current efficiency of 4.4 cd A⁻¹, and a low turn-on voltage of 3 V. More importantly, the operating lifetime for the QLEDs with double-sided MO NPs as CTLs is about 20 times longer than that of the PEDOT:PSS-based QLEDs. These results mark as a further step towards the practical application of the QLED technology.

3.2 Experiment Details

3.2.1 Synthesis of Green CdSe/ZnS QDs and ZnO NPs

Green-emitting CdSe/ZnS QDs with a chemical-composition gradient were prepared according to a modified method reported in the literature [8]. For a typical preparation of green-emitting QDs, 0.1 mmol of cadmium oxide (CdO), 4 mmol of zinc acetate ($\text{Zn}(\text{Acet})_2$), 5 mL of oleic acid (OA) were loaded in a 50 mL 3-neck flask, heated to 150 °C under vacuum to form cadmium oleate ($\text{Cd}(\text{OA})_2$) and zinc oleate ($\text{Zn}(\text{OA})_2$). Then 20 mL of 1-octadecene (1-ODE) was added to the reaction flask and the reactor was then filled with nitrogen and heated up to 300 °C. At the elevated temperature, 1.6 mL of tri-n-octylphosphine (TOP) dissolving 0.15 mmol of selenium (Se) and 4 mmol of sulphur (S) was quickly injected into the flask, and the reaction mixture was maintained at 300 °C for 10 min for the QD growth. To purify the synthesized QDs, the reaction mixture was cooled down to room temperature, and the QDs were extracted by the addition of acetone and methanol, followed by centrifugation. The CdSe/ZnS core-shell QDs were readily dispersed in toluene and have a photoluminescence quantum yield of ~70% in solution.

The precursor solution for ZnO nanoparticle layer was prepared according to a previously reported method [12]. For a typical synthesis, zinc acetate in dimethyl sulfoxide (DMSO) (0.1 M, 30 mL) and tetramethylammonium hydroxide (TMAH) in ethanol (0.55 M, 30 mL) were mixed and stirred for 1 h in ambient air. The ZnO NPs were washed twice and finally dispersed in ethanol, yielding a concentration of ~ 20 mg mL⁻¹.

3.2.2 Fabrication of QLEDs with WO₃ Nanoparticles as HTL

The patterned ITO substrates were cleaned by sonication sequentially in nonionic detergent, de-ionized water, acetone, and isopropyl alcohol (15 min each). The solution-processed WO₃ interfacial buffer layer was spin-coated on the O₂-plasma treated ITO substrate from 1.25wt% of diluted WO₃ ethanol solution at 5000 r.p.m. for 60 s, followed by thermal annealing at 80-110 °C for 30 min in a nitrogen glove box. The 2wt% of poly-TPD (ADS 254BE, dissolved in chlorobenzene) was spin-coated on the WO₃ layer at 4000 r.p.m. for 60 s and annealed at 150 °C for 30 min. Next, the QD film as the emissive layer was deposited on the ITO/WO₃/poly-TPD layer by spin-coating the QD toluence solution at a rate of 1000 - 4000 r.p.m. for 60 s, and baked at 90 °C for 30 min (the QDs were dispersed in toluene with a concentration of 15 mg/mL after the removal of the excessive organic ligands by successive centrifugation). After that, the 2, 2', 2''- (1, 3, 5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole) (TPBi, 35 nm), LiF (0.5 nm), and Al (190 nm) layers were thermally deposited under a base pressure of $\sim 2 \times 10^{-4}$ Pa. For the deposition of Al cathode, a shade mask was used to define the top contact and form an active device area of 9 mm². WO₃ dispersion in ethanol (2.5wt%) was purchased from Nanograde GmbH (product no. 4035). For the reference QLEDs using PEDOT:PSS as HIL, we followed the same procedure and the WO₃ nanoparticle layer was replaced by PEDOT:PSS (40 nm) which was spun on the ITO substrate at 4000 r.p.m. for 60 s and annealed at 150 °C for 30 min.

3.2.3 Fabrication of QLEDs with Doubled-sided MO NPs as CTLs

For the doubled-sided MO NPs-based QLEDs, the layers of WO₃ NPs, poly-TPD, QDs, and ZnO NPs were sequentially deposited on ITO by solution-processing. First, the pre-patterned indium tin oxide (ITO) glass substrates were thoroughly cleaned, followed by using the O₂-plasma treatment. Second, in the nitrogen glove box, the WO₃ NPs was spin-coated at 5,000 r.p.m. on the ITO substrate and baked at 100 °C for 30 min, followed by spin-coating a layer of poly-TPD, which was then annealed at 150 °C for 30 min. The QDs toluene solution (15 mg/mL) was then prepared on top of the HTL by spin-coating at 2,000 r.p.m., followed by annealing at 90 °C for 30 min. Subsequently, the ZnO nanoparticle film as the ETL was prepared by spin-coating the ZnO NPs dispersed in ethanol at a speed rate of 1,000 r.p.m. on top of the QDs layer. Next, the multilayer samples were loaded into the high-vacuum deposition chamber (at a pressure of $\leq 2 \times 10^{-4}$ Pa) to thermally deposit the Al electrode.

In addition, we also fabricated a control device for comparing the device performance, in which the MO NPs layers were substituted by thermal evaporation and sputtering. The optimized WO₃ was thermally evaporated on ITO substrate as the HTL in a deposition chamber, and the ZnO ETL was deposited onto QDs by radio frequency magnetron sputtering at room temperature using a metallic zinc target in a gas mixture of argon and oxygen.

3.2.4 Characterization

Atomic force microscopy (Cypher AFM, Asylum Research) was used to obtain the surface morphologies of the spin-coated WO₃ and ZnO NPs layers. UPS was performed using X-ray Photoelectron Spectroscopy (XPS) (VG Escalab 220i XL) with a He I (21.2 eV) gas discharge lamp. The EL spectra of

the fabricated WO₃ based QLED devices were measured using a PR650 Spectra Scan spectrometer or a Photo Research PR705 Spectra Scan spectrometer, while the luminance-current density-voltage (L-J-V) characteristics were obtained simultaneously by connecting the spectrometer to a programmable Keithley 236 source measurement unit.

The EL spectra of the double-sided metal-oxide NPs based QLED devices were measured using a Photo Research PR705 Spectra Scan spectrometer, while the luminance-current-voltage characteristics of the devices were measured simultaneously with a programmable Yokogawa GS610 source meter and a Konica Minolta luminance meter LS-110 in air at room temperature. All measurements were carried out at room temperature under ambient conditions without any encapsulation.

3.3 Results and Discussion

3.3.1 QLEDs with Solution-processed WO₃ NPs as HTL

The standard structure of QLEDs (reference device) is given as a multilayer structure of ITO/PEDOT:PSS/poly-TPD/QDs/(TPBi)/LiF/Al [22,24]. The CdSe/ZnS core-shell structured QDs prepared according to a previous reported literature were used for the emissive layer [8], and the poly-TPD and TPBi layers served as the hole transport layer (HTL) and the electron transport layer (ETL), respectively. In our case, the WO₃ nanoparticle layer spin-coated on ITO was used to replace PEDOT:PSS as the HTL/HIL. The device structure is schematically presented in Figure 3-1a. The atomic force microscopy (AFM) image of the close-packed thin film of WO₃ NPs on ITO with an average particle size of 7 nm (annealed at 100 °C in the glove box) is shown in Figure

3-1b. The surface roughness (RMS) of the film made from a 2wt% of WO_3 ethanol solution is only 2.8 nm, indicating that the nanoparticle film has a smooth surface. To confirm the electronic structure of the as-prepared WO_3 nanoparticle film, the ultraviolet photoelectron spectroscopy (UPS) spectra including the magnified regions of the photoemission cut-off and valence band are given in Figures 3-1c and 3-1d. The photoemission onset is found at 16.05 eV from the photoemission cut-off in Figure 3-1c. This corresponds to a work function (WF) of 5.15 eV, in agreement with the WF values of WO_3 reported in literature, which can range from 4.7 to 6.4 eV depending on the film preparation conditions [111]. Figure 3-1d displays the zoom-in spectra of the density of states near the oxide valence band edge and the ionization energy (IE) of the WO_3 film that is determined to be 2.7 eV with respect to the Fermi level. According to the schematic energy level diagram of the device depicted in Figure 3-1e, it can be observed that the electrons can easily be injected from the Al to the QD layer. However, the case is quite different for the hole injection [95,108,110]. For n-doped WO_3 or MoO_3 , the hole injection from ITO to the organic semiconductors results from electron extraction from the highest occupied molecular orbital (HOMO) level of organic semiconductors through the WO_3 or MoO_3 conduction band, and then into ITO. For our case, owing to the deep lying electronic states of WO_3 nanoparticle interface layer, the energy barrier for the injection of electrons from the HOMO level to the conduction band of WO_3 NPs is quite small, and the efficient hole injection can be proceeded via electron extraction from the HOMO level of poly-TPD into the conduction band of WO_3 NPs.

Figure 3-1. (a) Schematic of the WO₃ NP-based QLED configuration. (b) AFM image of WO₃ nanoparticle layer deposited on ITO substrate. UPS spectra of a WO₃ nanoparticle film annealed at 100 °C including (c) secondary-electron cutoff and (d) zoom-in section of the evolution of the density of states near the oxide valence band edge. (e) Energy level diagram of the QLEDs using WO₃ NPs as HIL.

Figure 3-2a presents the output performance of an optimized WO₃ NP-based QLED. The device is fabricated with QDs of 4 monolayers-equivalent thickness (~20 nm) and a WO₃ nanoparticle film of 2 monolayers-equivalent thickness (~14 nm). The electroluminescence (EL) spectrum of the QLED was recorded at the bias voltage of 12 V, showing a characteristic QD EL peak centered at ~518 nm with a full width at half maximum (FWHM) of ~30 nm. It should be noted here that there is a weak emission in the blue-wavelength region due to the residual emission from poly-TPD. The emission from poly-TPD indicates the possible imbalance of the charge in the QD layer. The

electrons on the lowest unoccupied molecular orbital (LUMO) of TPBi can jump over the 0.9 eV energy barrier into the LUMO of poly-TPD through defects of the QD layer to combine with holes in the poly-TPD layer. This phenomenon can be observed in almost all PEDOT:PSS-based QLEDs. Figure 3-2b shows the luminance and current density characteristics of the device as a function of the applied voltage. The luminance-current density-voltage characteristics show a low turn-on voltage of 3.6 V and a peak luminance of 3565 cd/m² at a current density of 444.44 mA/cm². The maximum EQE of 0.43% was obtained under the same current density.

Figure 3-2. (a) EL spectrum and (b) current density-voltage (J-V) and luminance-voltage (L-V) characteristics of QLED.

To further improve the performance of WO₃ NP-based QLEDs, we deposited a 2,2',2''-tris-(N-carbazolyl)-triphenylamine (TCTA) electron-blocking layer (EBL) on the QD layer to suppress the excess electrons for improving the charge balance of device. The LUMO of TCTA is 2.4 eV [112] and the relatively high energy barrier of 0.8 eV between the LUMO of TCTA and that of TPBi can block electrons to reach the poly-TPD layer in the device effectively. Figure 3-3 shows the EL spectra for the device with TCTA utilized as the EBL under different driving currents. It can be observed that the blue emission of poly-TPD is hardly found even in the case of a high driving current, as electrons from TPBi are completely blocked by the TCTA EBL before jumping into the LUMO of poly-TPD. This is another advantage of using TCTA because the blue emission from poly-TPD degrades the colour purity.

Figure 3-3. EL spectra of the device at different injection currents (inset shows the schematic cross section of the device structure used in this study).

Figures 3-4a and 3-4b show a comparison of the luminance-current density (L - J) and efficiency-current density (E - J) characteristics of the WO₃

NP-based QLED and an optimized PEDOT:PSS-based QLED with the same structure. As can be seen, the two devices show a similar trend in the L - J and E - J characteristics, as the driving current is increased. However, compared with the original QLEDs without the TCTA used as the EBL, the performance of QLED with TCTA increases significantly, showing the maximum luminance, EQE and current efficiency values of 30,006 cd m^{-2} and 3.32%, respectively. To the best of our knowledge, the EQE of 3.32% is much higher than the previously reported values for green QLEDs with normal architecture (the recently reported green QLEDs using the inverted architecture reached an EQE level of 5.8% [22]). Table 3-1 summarizes the key figure-of-merits of the two QLEDs. The maximum brightness, EQE, current efficiency and efficacy for the WO_3 NP-based QLED are superior. Also, the turn-on voltage of the WO_3 NP-based QLED decreases to 3.8 V, which is lower than that observed for the PEDOT:PSS-based device (4.2 V). Moreover, it can be noted that the WO_3 NP-based QLED still works well even under the current of 50 mA, while the PEDOT:PSS-based QLED has burned down when the driving current is just 40 mA, which indicates the better device stability for the WO_3 NP-based QLED.

Figure 3-4. (a) Luminance-current density and (b) external quantum efficiency (EQE)-current density characteristics of the resulting QLEDs using PEDOT:PSS and WO₃ NPs as HTLs, respectively.

Table 3-1. List of figure-of-merits to compare the device performance using WO₃ nanoparticles (A) and PEDOT:PSS (B) as HILs.

Device	$V_{\text{turn-on}}$ [V]	Max. Luminance [cd/m ²]	Max. EQE [%]	Max. Current efficiency [cd/A]	Max. Efficacy [lm/W]	Lifetime [s]
A	3.8 V	30,006 (50 mA)	3.32	9.75	6.8	6530
B	4.2 V	25,202 (40 mA)	3.02	8.74	6.0	3130

Figure 3-5 shows the operating stability of the resulting unencapsulated WO₃ NP-based QLED in comparison with the optimized PEDOT:PSS-based QLED. Under a continuous current driving condition corresponding to an initial luminance of 1000 cd/m², it can be clearly observed that using WO₃ NPs to replace PEDOT:PSS as the HILs in QLEDs can drastically improve device stability. The unencapsulated WO₃ NP-based QLED displays a half-lifetime of

6530 s, showing an approximately two-fold lifetime enhancement as compared to that of PEDOT:PSS-based QLED. The significant improvement in the device stability can be attributed to the fact that WO_3 NPs are highly stable when compared to organic materials and can therefore act as a protection layer for organic materials.

Figure 3-5. Operating lifetime characteristics of the resulting WO_3 NP-based QLED and the optimized PEDOT:PSS based QLED. The luminance of these QLEDs was measured without using encapsulation and during the continuous operation at a constant current density corresponding to an initial luminance of 1000 cd/m^2 . Both types of QLEDs were fabricated using the same device architecture.

3.3.2 QLEDs with Double-sided MO NPs as CTLs

The device architecture of MO NP based QLED is schematically shown in Figure 3-6a. Specifically, the multilayered structure of ITO/ WO_3 NPs/poly-TPD/QDs/ZnO NPs/Al is used here, in which ITO serves as the anode, WO_3 NPs and poly-TPD as the HTLs, ZnO NPs as the ETL and Al as the cathode.

Figure 3-6b illustrates the corresponding energy level diagram of MO NP based QLED. As can be seen, the hole transport material poly-TPD has a large band gap, which block the possibility for electrons from the LUMO level of QDs to be collected at the ITO anode. The efficient hole injection into QDs can be enabled by the electron extraction from the HOMO level of poly-TPD through the WO_3 conduction band, and then into ITO. For the ZnO ETL, due to the low band offset for Al/ZnO and small energetic barrier with QDs, the electron transport and injection into QDs are quite efficient. Meanwhile, ZnO with a large band gap and low valence band level is also favorable for exciton blocking [7].

Figure 3-6. (a) Schematic diagram of multilayer MO NP-based QLEDs. (b) Energy level diagram of the MO NP-based QLEDs.

In the fabrication of QLED, the morphology of thin film layers can affect device performance significantly. Therefore, a smooth surface is essential for obtaining high-performance device. According to the three-dimensional atomic force microscopy (AFM) images shown in Figure 3-1b, the surface RMS of the WO₃ NPs layer on top of the ITO electrodes is found to be quite small, which is the advantage for the deposition of smooth self-assembled QDs onto the WO₃. Figure 3-7 presents the AFM image of uniform ZnO NPs as ETL on top of the tri-layer structure (WO₃ NPs, poly-TPD and QDs) with an RMS value of 2.6 nm, which relies on compatibility of the QDs with NPs surfaces. Noted that the average diameter for ZnO NPs used here is around 3-5 nm [12].

Figure 3-7. AFM images of spin-coated ZnO NP layers on the top of multilayered structure of ITO/WO₃/poly-TPD/QDs.

Figure 3-8a shows the selected QDs solution photoluminescence (PL) and characteristic EL spectra of MO NP-based QLED at an applied voltage of 10 V. The saturated emission band in EL spectrum is centered at $\lambda = 516$ nm with a full width at half maximum (FWHM) of 43 nm. However, there is a slight red shift and broadening for EL relative to PL. Excited by $\lambda = 400$ nm UV light, the PL emission band peaking at 507 nm is observed with the FWHM

of 33 nm. The difference between the EL and PL emission wavelengths can be attributed to the combination of Förster energy transfer, dielectric dispersion and electric-field-induced Stark effect [6,18,113]. Specifically, the energy transfer from NPs to the larger particles in the agglomerate arising from spin-coating process, thus the red shift of EL peak is observed [114,115]. The Stark effect is responsible for the Stark broadening of spectral lines by charged particles. In addition, the comparisons of the EL with the PL spectrum confirm that the EL of this device originates from the green CdSe/ZnS QDs, and there is no emission from adjacent poly-TPD layer, which indicates that the device emission is due completely to the QDs. The results can be attributed to the balance charge carrier within the devices. Moreover, because of the facilitated hole injection from WO₃ NPs and poly-TPD as well as electron injection into QDs from ZnO NPs, the carrier recombination within QDs layer becomes more direct and efficient. This is beneficial to the pure emission solely from QDs enabling spectrally pure QLED. Figure 3-8b displays the photograph of MO NP-based QLED at an applied voltage of 5 V, which exhibits a bright and saturated green emission.

Figure 3-8. (a) Normalized PL and EL spectra of QDs and MO NP-based QLED, respectively. (b) The photograph of MO NP-based QLED at an applied voltage of 5 V.

Figure 3-9a presents the luminance and current density curves as a function of voltage for MO NP-based QLED. This device shows a low turn-on voltage of 3 V, measured using a high-sensitivity spectrometer. The results confirm the minimized barrier height for charge injection into the device, and then electrons and holes can be efficiently injected into the QDs even at low driving voltages. From the L - V characteristic, it yields a peak luminance of $21,300 \text{ cd m}^{-2}$ at the applied voltage of 10 V. Figure 3-9b illustrates the performances in terms of CE - EQE - V trends of the MO NP-based QLED. The maximum CE and EQE of the resulting device were measured to be 4.4 cd A^{-1} and 1.3% at the applied voltage of 10 V, respectively, representing a more than 10-fold improvement over the previously reported structures of all-organic and all-inorganic based QLEDs [38,91,116].

Figure 3-9. (a) L - J - V curve of MO NP-based QLED. (b) Characteristics of MO NP-based QLED in terms of CE - EQE - V .

As shown above, the hybrid QLED based upon the double-sided inorganic MO NP CTLs is demonstrated with excellent optical properties. Furthermore, the comparative experiments are carried out to demonstrate the superiority of solution-processed WO_3 and ZnO NPs CTLs. Thus the control device is designed and fabricated, in which the optimized WO_3 and ZnO layers are thermally evaporated (5 nm) and sputtered (50 nm), respectively. As shown in Figure 3-10a, the peak luminance and EQE of 2,855 cd m^{-2} and 0.28% are recorded for the optimized control device. Due to the nonradiative

recombination of the excessive carriers (holes or electrons), a dramatic decrease in luminance and EQE are observed. Figure 3-10b plots the J - V behaviors of the MO NP-based QLED and the control device. Since the control device suffers from a greatly unbalanced charge recombination, the turn-on voltage of 6 V is double of that observed in MO NP-based QLED. Obviously, the performance of MO NP-based QLED is much superior to that with thermally evaporated WO_3 and sputtered ZnO layers.

Figure 3-10. (a) Characteristics of control device in terms of L - EQE - V . (b) J - V behaviors of MO NP-based QLED and control device.

The functions of the WO₃ and ZnO NPs can be explained in five ways:

1) Solution-processed WO₃ and ZnO NPs layers are compatible with QDs to fabricate a bright and stable QLED. 2) The WO₃ NPs can effectively improve the hole collection at the interface between the ITO electrode and the active layer [95]. 3) The ZnO NPs layer acts as an optical spacer and simultaneously an exciton blocking layer, improving electron injection in the QDs layer. 4) The solution processed ZnO NPs ETLs does not affect the below QD layer while the sputtering process often damages the QDs layer to a certain extend. 5) The efficient carrier recombination within QDs layers occurs owing to the facilitated charge carrier injection into QDs from WO₃ and ZnO NPs layers, as well as the enhanced charge carrier balance within the devices. All of effects have great influences on enhancing charge recombination in the QDs layer.

The luminance variation is displayed as a function of time in Figure 3-11. The lifetime test of the double-sided inorganic MO NP-based QLED is performed by operating the device under N₂ atmosphere (oxygen concentration: ≤ 20 ppm) at a constant brightness level of 600 cd m⁻² [117]. The non-inverted QLED using a standard device structure (ITO/PEDOT:PSS/poly-TPD/QDs/1,3,5-tris(Nphenylbenzimidazol-2,yl)benzene/LiF/Al) shows a rapid deterioration at an initial luminance of 600 cd m⁻² within 4 h of continuous operation. On the contrary, the brightness of MO NP-based QLED decays slowly to a half of its initial value after 95 h. It is obvious that this device with double-sided MO NPs as CTLs is more stable under continuous operation and the lifetime is almost 20-folds higher than that of the standard device. The improvement in the device stability, in agreement with the low turn-on voltage and high EQE, suggests the facilitated hole and electron injection from charge

transport layers (hole and electron transport layers with lower HOMO and higher LOMO levels, respectively) into QDs, which improves the charge carrier balance within the devices during operation.

Figure 3-11. Lifetime characteristics of MO NP-based and standard QLEDs.

3.4 Conclusion

In conclusion, we have demonstrated an efficient QLED using a solution-processed WO_3 nanoparticle film instead of using PEDOT:PSS as the anode interfacial buffer layer. The WO_3 NP-based QLEDs show enhanced performance as compared to the PEDOT:PSS-based QLEDs. The device performance for the green QLEDs using a non-inverted structure matches that of the best QLEDs with organic materials used as HTLs/HILs. Moreover, with the incorporation of the WO_3 NPs, the device exhibits a significant improvement in the device stability and the lifetime is increased by approximately two folds at an initial brightness of 1000 cd/m^2 compared to that of PEDOT:PSS-based QLEDs. Meanwhile, since the solution-processed preparation method of WO_3 nanoparticle film used in our work is very simple

and can be achieved at low annealing temperatures, it is suitable for application in flexible devices where the flexible substrates such as plastics often cannot withstand high annealing temperatures.

Besides, this work further fabricated a bright, stable and all solution-processed QLED with double-sided MO NPs as CTLs (WO_3 NPs and ZnO NPs as the HTL and the ETL, respectively). The resulting QLED exhibits an excellent device performance, with a peak luminance of $21,300 \text{ cd m}^{-2}$, the maximum CE of 4.4 cd A^{-1} , a low turn-on voltage of 3 V, and a long operating lifetime. The enhanced device performance can be mainly attributed to the use of inorganic MO NPs as CTLs and the compatibility of WO_3 and ZnO NPs layers to QDs, which facilitate the charge carrier injection into QDs and improve charge balance of QD layer.

These results indicate that the solution-processed WO_3 and ZnO NPs can serve as excellent HTL and ETL thin films and offer a practicable platform for the realization of high-performance, stable and large-area commercial QLEDs using a low-cost manufacturing process.

Chapter 4 Preparation of High-quality InP/ZnS Quantum Dots and Their Applications in Quantum Dot Light Emitting Diodes

4.1 Introduction

Semiconductor nanocrystals (NCs), also known as colloidal quantum dots (QDs), exhibit unique size dependent properties and have attracted considerable interest thanks to their promising applications including light emitting diodes (LEDs) [6,9,17], lasers [26,118-121], biomedical imaging [122-124], and sensors [31,125-128]. Currently, CdSe NCs as the workhorse have been well developed for such uses. Despite their apparent advantages such as high emission quantum yields, narrow emission linewidth and good photostability [129-132], the intrinsic toxicity of CdSe NCs makes them environmentally restricted, which has thus cast a doubtful future for their practical applications [34,133,134]. Indium phosphide with a band gap of 1.35 eV is considered as the ideal alternative material, which offers a similar emission wavelength range but without intrinsic toxicity [135-145]. Previous studies have shown that InP NCs can be well used in white LEDs for improving their colour rendering index (CRI). For example, Nann *et al.* reported a solid-state white LED with a CRI of 86 by the addition of InP/ZnS NCs into green together with yellow phosphors [146]. Recently, a quantum efficiency (QE) of 85% for InP based NCs was realized [147], and electroluminescence (EL) emission from InP-based NCs was also demonstrated [68,148]. However, there exist crucial problems related to the performance of InP based NCs. Among them are their colour purity and emission spectrum tunability, which are much

inferior to the well-developed CdSe NCs. The inferior properties of these InP NCs can be attributed to a harsh reaction control due to the strong coordinating strength of indium ligands. The emission linewidth for the typical InP NCs is much wider (50 - 80 nm) than that of CdSe NCs (15 - 40 nm), which leads to a worse colour purity for InP as compared to CdSe. A pioneer work on the synthesis of the InP/ZnS NCs with tunable emission wavelength has been reported by Nann' group [149]. Although an impressively wide emission spectrum tunability can be achieved from their method, the synthesis procedure used is quite complicated, which requires continuous multiple injections for preparing NCs with emission at longer wavelengths. As a result, it is still a great scientific challenge to obtain InP based NCs with photometric performance as good as CdSe ones.

In this chapter, we report on the controlled synthesis of high-quality InP/ZnS NCs with a core-shell structure by a facile one-pot solvothermal method. The resulting cadmium-free NCs show high quantum yields (above 60%), wide range spectrum tunability, narrow emission linewidths, and excellent photostability. The PL spectrum of the NCs can be tuned to cover the entire visible spectrum only by changing the ratio of InP:ZnS without multiple injections. The photoluminescence full width at half maximum (FWHM) of 38 nm presented in this work is the narrowest linewidth reported for InP-based NCs to date. Besides, making use of the red emitting InP/ZnS NCs, a hybrid white QLED has been demonstrated with a high CRI of 91.

4.2 Experiment Section

4.2.1 Fabrication of QLED Devices

The patterned indium tin oxide (ITO) substrates were thoroughly cleaned by sonication sequentially in detergent, de-ionized water, acetone, and isopropyl alcohol for 15 min each, followed by an O₂ plasma treatment. The poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was first spun on the plasma-O₂-treated ITO substrate at a spin rate of 4000 r.p.m. for 60 s and annealed at 150 °C for 30 min in a N₂-filled glove box. The 1 wt % of poly(N,N'-bis (4-butylphenyl)-N,N'-bis(phenyl)benzidine) (poly-TPD) dissolved in chlorobenzene was then spin-coated on the PEDOT:PSS film at 2000 r.p.m. for 60 s, followed by thermal annealing at 110 °C for 30 min. After that the QD layer was deposited on the ITO/PEDOT:PSS/poly-TPD layer by spin-coating the InP/ZnS NCs toluene solution with a concentration of 10 mg/ml at a rate of 1000 - 2000 r.p.m. for 60 s, and baked at 60 °C for 30 min. Subsequently, the samples were loaded into a high-vacuum deposition chamber (at a based pressure of $\leq 2 \times 10^{-4}$ Pa) to thermally deposit the TPBi (35 nm), LiF (0.5 nm), and Al (150 nm) layers.

4.2.2 Characterization

Transmission electron microscopy (TEM) characterization was performed with a transmission electron microscopy (JEOL, JEM-2010) operating at 200 kV. Samples for TEM analysis were prepared by drying a drop of InP/ZnS NCs dispersed in toluene on amorphous carbon-coated copper grids. The Energy-dispersive X-ray spectroscopy (EDS) was obtained using a field emission scanning electronic microscopy (FESEM, JEOL JSM-6340F). The photoluminescence (PL) spectra were recorded in the spectral range of 350 - 800 nm at room temperature (Fluorolog-3 Spectrofluorometer). The absorption

spectra were obtained over a tunable wavelength range from 350 to 750 nm using a UV-vis spectrophotometer (Shimadzu) with a 50 W halogen lamp and a deuterium lamp as the excitation source. The fluorescence QY of InP/ZnS NCs was measured by comparing the integrated area of PL emission of rhodamine 6G in ethanol (QY=95%) with InP/ZnS NCs toluene solution, with the same absorbance value at excitation wavelength and similar fluorescence emission wavelength. The electroluminescence (EL) spectra of the resulting devices were measured using a PR650 Spectra Scan spectrometer, while the luminance-current density-voltage (L-J-V) characteristics were obtained simultaneously, by connecting the spectrometer to a programmable Keithley 236 source measurement unit.

4.3 Results and Discussion

4.3.1 Synthesis and Properties of InP/ZnS Core-shell QDs

For a typical synthesis, 0.3 mmol of In(MA)₃, 0.3 mmol of P(TMS)₃ and 3mL of ODE were fully mixed in a nitrogen glove box at room temperature (following which the colour of solution quickly change from colourless to yellow due to the nucleation process of InP). Next, the as-prepared InP nuclei solution was transferred into a three-neck flask (50 ml), and then 0.3 mmol of zinc stearate and 21 mL of ODE were added into the reaction system. The mixture was heated to 260 - 300 °C quickly with strong agitation under Ar atmosphere and kept for a certain time (10 - 30 min) to grow InP cores with Zn-rich surface. Subsequently, 0.3 mmol of 1-dodecanethiol (DDT) or S powder was added into InP core-containing solution which was cooled down to 60 °C around beforehand, and was repeatedly heated up to 300 °C for 10 min for

growing ZnS shell. After that, an additional ZnS shell can also be obtained by the decomposition of zinc diethyldithiocarbamate. The resulting precipitate was dispersed in toluene. The process is illustrated in Figure 4-1a. By precisely adjusting the ratio of InP:ZnS, the the full colours in visible range have been achieved in our present work. The corresponding image of these QD samples with different ratios of InP:ZnS excited by UV light is shown in Figure 4-1b.

Figure 4-1. (a) Schematic of the synthetic procedure of InP/ZnS NCs. (b) Photograph of the samples with different ratios of InP:ZnS excited by UV light.

Figure 4-2a shows the representative low-magnification transmission electron microscopy (TEM) image of the resulting InP/ZnS NCs. It can be seen that these resulting NCs with an average diameter of ~5 nm are quite uniform and well-dispersed. The energy-dispersive X-ray spectroscopy (EDS) spectra in Figures 4-2b and 4-2c were taken from the as-prepared InP nuclei and the resulting InP-ZnS core-shell structured NCs, respectively. The EDS spectrum of the as-prepared InP nuclei indicates that no element are introduced except In and P elements (Figure 4-2b). After coating ZnS shell, the EDS spectrum in

Figure 4-2c shows that the presence of Zn and S elements, which further suggests that the successful synthesis of InP QDs with ZnS shell.

Figure 4-2. (a) TEM image of the resulting InP/ZnS NCs at low magnification. The inset in (a) illustrates the core-shell structure of InP/ZnS NCs. Here the red region represents InP core, and the green part show ZnS shell. EDS of (b) InP nuclei and (c) the resulting InP/ZnS NCs. The samples were tested on a quartz substrate (main component: SiO_2).

Figure 4-3 shows the UV-vis absorption and PL spectra of the as-grown InP/ZnS NCs prepared at 300 °C. It can be observed that both the absorption and PL spectra red-shift toward longer emission wavelengths with the increase of the molar ratio of InP:ZnS from 1:2 to 16:1. It has been found that the addition of zinc carboxylates not only acts as the zinc sources in the synthesis of InP NCs but also influences the growth process of NCs by stabilizing the surfaces of particles and reduces the critical nucleus size [145]. For our case,

the absorption spectra and PL emission wavelength can be continuously tuned from blue to near-infrared (NIR) region by increasing the ratio of InP precursors to zinc stearate while keeping the other reaction conditions unchanged. In addition, the zinc-rich surface of InP cores is beneficial to grow the ZnS shell, after adding the precursor of S, a homogeneous ZnS shell can be formed on the InP cores (the core-shell structure can improve the fluorescence quantum yield of NCs). Note that the addition of zinc stearate cannot result in lattice doping because the bulk zinc doping of InP or preparation of Zn_3P_2 requires very harsh reaction conditions such as reactive zinc precursors, high temperature and a long reaction time [34,149,151].

Figure 4-3. UV-Vis absorption and PL spectra of the resulting InP/ZnS NCs with different ratios of InP:ZnS (increasing the ratio of InP to ZnS from left to right). The PL and absorption spectra of NCs were red-shifted successively.

The QY and FWHM of the resulting InP/ZnS core-shell NCs are shown in Figure 4-4. We can see that a high fluorescence QY and narrow emission linewidth are obtained when the ratio of InP to ZnS is lower than 1.2:1, and the maximum QY reaches 60.2 %, which is comparable to that of CdSe NCs. The observed high fluorescence QY can be attributed to the effective passivation of the surface-state traps of the NC cores in terms of the strain-relieved shells. With further increasing the ratio of InP to ZnS, the QY of NCs decreases gradually due to the decreased amount of ZnS precursor that the formed thin ZnS shell cannot effectively passivate the surface of InP cores. At the same time, the FWHM of the resulting InP/ZnS NCs is also broadened with the decrease of amount of zinc stearate, which can function to stabilize the NC growth and produce a narrow particle size distribution.

Figure 4-4. Evolution of fluorescence QY and FWHM of InP/ZnS NCs with different ratios of InP:ZnS (increasing the ratio of InP to ZnS from left to right).

The optical property of semiconductor NCs strongly depends on their surface ligands. It has been found that most of surface ligands show stronger coordinating strength towards indium than cadmium [148]. The presence of

strong ligands for indium can result in unstable initial nuclei, and even particle growth at low temperature. To reduce the negative influence of strong coordinating ligands, we deliberately designed a preliminary step in the nanocrystal synthesis: the InP nuclei was grown by mixing the In(MA) and $P(TMS)_3$ in a non-coordinating solvent (1-octadecene in our present study), as evidenced by the colour change of the reaction solution from colour to yellow when the In(MA) and $P(TMS)_3$ were mixed. From Figure 4-5a, it can be observed that the PL emission wavelength is obviously shorter when the sample was prepared through the preliminary step in a non-coordinating solvent, which suggests that the growth rate of NCs was slower under such reaction condition. Therefore, it could be reasonably concluded that the more stable synthesis process due to the slow growth of NCs would favor the formation of NCs with a narrow size distribution.

On the other hand, an excess of indium precursor was required for avoiding the surface defects and aggregation of InP nuclei caused by the lack of surface ligands in the preliminary reaction system. The excess indium provides an In-rich surface, allowing a sufficient amount of ligands to bind. As shown in Figure 4-5b, we can observe that there is a deep-trap surface emission at 630 nm appeared because of the dangling indium bonds in the sample with In:P ratio of 1:1. In this case, the fluorescence QY of the resulting NCs is quite low ($\sim 7.2\%$) because of the presence of the large amount of surface defects in NCs that give rise to nonradiative recombination processes. With the increase of In ratio (In:P=1.18:1), the defect emission in NCs disappears and the QY is dramatically enhanced ($\sim 50\%$). Meanwhile, the FWHM of the resulting NCs is remarkably narrowed (only 38 nm), indicating the high colour purity of the

resulting NCs. It can be worth mentioning that literature data related to the FWHM of InP-based NCs is typically wider (50-80 nm) than that of CdSe (15-40 nm) while the emission linewidth of 38 nm reported in this work is very close to that of CdSe NCs.

Figure 4-5. PL spectra of (a) the resulting InP/ZnS NCs prepared through a preliminary step (black dots) and without preliminary step (red dots) and (b) the samples prepared with different ratios of In:P.

The ZnS shell can play an important role in improving the fluorescence QY of InP NCs. However, with the increase of InP:ZnS ratio, the reduced amount of ZnS is too low to passivate the InP cores well, which leads to a quick decrease of QY. To solve the problem, an additional ZnS shell is coated on the initial InP/ZnS NCs with a thin ZnS shell by a one-step single source precursor injection. It can be observed from Figure 4-6a, the fluorescence QY for the initial red emitting NCs with thin ZnS shell is 12.3%, after growing an additional ZnS shell, the QY of the sample is increased to 38.1%.

Another serious negative influence caused by the thin ZnS shell is the poor photostability for the resulting NCs. As the amount of Zn precursor used

constantly reduces, the ZnS shell would become very thin. Such a thin shell is very vulnerable against degradable conditions, resulting in the dramatic reduction in the photostability, which could be examined by continuous irradiation with UV light. Figure 4-6b shows a rapid decrease in PL intensity for the NCs without additional ZnS shell (which decreases to 70% of its initial value) within 10 h of UV irradiation (365 nm, 3 mW/cm²). In contrast, for the NCs with a thick ZnS shell, even after 25 h of continuous irradiation, little photodegradation can be observed.

Figure 4-6. (a) PL intensity and (b) photostability of the resulting InP/ZnS NCs with additional ZnS shell and without additional ZnS shell.

4.3.2 Application of InP/ZnS QDs in QLEDs

To assess suitability of the resulting InP/ZnS core-shell NCs as emitters for QLED application, a common QLED device structure of ITO/PEDOT:PSS/poly-TPD/QDs/TPBi/LiF/Al was fabricated, as schematically presented in Figure 4-7a. In the designed QLED structure, the QDs layer, spin-casted from the red emitting InP/ZnS NCs in toluene solution is used as the emissive layer (EML), PEDOT:PSS is as the hole injection layer (HIL), poly-TPD is as the hole transport (HTL), TPBi is as the electron transport layer (ETL), LiF is as the electron injection layer (EIL) and Al serves as cathode, which is deposited using a shade mask for defining the top contact and forming an active device area of 9 mm². The corresponding schematic energy level diagram of the resulting devices is depicted in Figure 4-7b, which shows that the electrons and holes can be injected from the Al to the QD layer and from the ITO to the QD layer, respectively.

Figure 4-7. (a) Schematic of QLED configuration based on InP-ZnS QDs. (b) Energy band diagram of the QLEDs using InP/ZnS QDs.

The QLED output spectrum is recorded at the bias voltage of 11 V (Figure 4-8a), exhibiting a broadband coverage over the entire visible wavelength regime. The red emission is attributed to the red-emitting InP/ZnS NCs (confirmed by the PL profile of red NCs), which is spectrally complementary to the blue-green emission of poly-TPD for white light generation. The CIE coordinates of the cadmium-free QLED is (0.332, 0.338), which is close to the balanced white coordinates (inset of Figure 4-8a). In addition, the white light of the QLED is characterized with a high CRI of 91, significantly higher than that of most of solid-state white LEDs. The typical current density and luminance curves as a function of applied voltage for the device are shown in Figure 4-8b. The maximum brightness for the resulting white QLED is 270 cd/m² and the turn-on voltage (V_T) is 7.5 V. The V_T is defined as the voltage at which the luminance is 1 cd m⁻². An image of the

white QLED output was recorded at the luminance of 270 cd/m^2 (Inset of Figure 4-8b), which displays bright and uniform white emission.

Figure 4-8. (a) EL spectrum of white QLEDs and PL spectrum of red-emitting InP/ZnS NCs. Inset: CIE chromaticity coordinate diagram of the white QLEDs. (b) Current density-voltage (J-V) and luminance-voltage (L-V) characteristics. Inset: a photograph of a QLED with a pixel size of 3 mm $\times$ 3 mm.

4.4 Conclusion

In conclusion, high-quality InP/ZnS core-shell NCs with luminescence tunable over the entire visible spectrum have been prepared by a facile one-pot

solvothermal method without multiple injections. The excellent optical properties of the resulting InP based NCs including high quantum yields, narrow emission linewidth and good photostability were obtained by effectively passivating the surface defects of InP NC cores with a strain-relieved ZnS shell. The FWHM of the NCs can be as narrow as 38 nm. Additionally, in this work, a white QLED based on the resulting red emitting NCs has been successfully demonstrated with a high CRI of 91. The high performance of the resulting InP based NCs coupled with their low intrinsic toxicity may further enable industrial applications of these NC emitters.

Chapter 5 Cadmium-free, Hybrid Organic/Quantum Dot Light Emitting Diodes

5.1 *Introduction*

The serious drawback of the present colloidal quantum dot light emitting diodes (QLED) technology is that it is heavily dependent on cadmium-based quantum dots, which has severely hindered the commercialization of the QLED technology [34,133]. Indium phosphide (InP) is considered as the ideal alternative, which offers a similar emission spectrum but without intrinsic toxicity [136-141]. In the past few years, the efficiency of InP-based QDs was improved significantly and the QLEDs with InP-based QDs have been also demonstrated [9,68,148,152]. However, the overall performance for InP-based QLEDs has been low and the QLEDs with efficient white emission have rarely been reported. On the other hand, some research groups have demonstrated that the combination of emission of organic molecules with QDs is quite promising for fabricating high-performance white hybrid QLEDs [1,9,69]. Nevertheless, much work is further needed in hybrid QLED research for improving device performance.

In this section, we demonstrate green InP-based QLEDs with a maximum brightness close to 700 cd/m^2 , accompanied with a relatively low turn-on voltage of 4.5 V, which is the best performance ever reported for InP-based QD LEDs. Meanwhile, with the fabrication of a loosely packed QD layer to form some direct contact between the hole-transporting layer (poly-TPD) and electron-blocking layer (TPBi), we demonstrated a ternary complementary white QLED with the blue emission from poly-TPD, green emission from QDs,

and the red exciplex emission between poly-TPD and TPBi. The resulting ternary complementary white QLEDs show good photometric performance with a high colour rendering index (CRI) of 95 and a moderate low correlated colour temperature (CCT) of 4710 K.

5.2 Experiment Details

5.2.1 Fabrication of Ternary Complementary QLED Devices

The patterned indium tin oxide (ITO) substrates were thoroughly cleaned by sonication sequentially in detergent, de-ionized water, acetone, and isopropyl alcohol for 15 min each, followed by an O₂ plasma treatment. The PEDOT:PSS was then spun on the plasma-O₂-treated ITO substrate at a spin rate of 4000 r.p.m. for 60 s, and dried at 150 °C for 30 min in a nitrogen glove box. Next, the 2 wt % of poly-TPD in chlorobenzene was spin-coated on the PEDOT:PSS layer at 2000 r.p.m. for 60 s, and annealed at 110 °C for 30 min. The QD layer was deposited on the ITO/PEDOT:PSS/poly-TPD layer by spin-coating the InP based QDs dispersed in toluene with a concentration of 5 mg/mL at a rate of 1000 – 4000 r.p.m. for 60 s, and baked at 60 °C for 30 min. After that, the samples were loaded into a high-vacuum deposition chamber (at a based pressure of $\leq 2 \times 10^{-4}$ Pa) to thermally deposit the TPBi (35 nm), LiF (0.5 nm), and Al (190 nm) layers. The active device area for the resulting QLED devices is 9 mm².

5.2.2 Characterization

The electroluminescence (EL) spectra of the fabricated devices were measured using a PR650 Spectra Scan spectrometer, while the luminance-

current density-voltage (L-J-V) characteristics were obtained simultaneously by connecting the spectrometer to a programmable Keithley 236 source measurement unit. The photoluminescence (PL) spectrum was recorded using a Shimadzu RF-5301PC spectrofluorophotometer equipped with a 150 W Xenon lamp as the excitation source. Transmission electron microscopy (TEM) characterization was performed with a transmission electron microscopy (JEOL, JEM-2010) operating at 200 kV. The Energy-dispersive X-ray spectroscopy (EDS) was obtained using a field emission scanning electronic microscopy (FESEM, JEOL JSM-6340F). Atomic force microscope (Cypher AFM, Asylum Research) was used to image the QD layer. All measurements were carried out at room temperature under ambient conditions.

5.3 Results and Discussion

5.3.1 Synthesis and Properties of InP/ZnSeS Core-shell QDs

For the present work, the InP/ZnSeS core-shell structured QDs used here were prepared by a modified literature procedure [137]. A typical procedure is given as follows: 1 mL of In(OA)₃ solution, 0.25 mL of Zn(OA)₂ solution, and 7.5 mL of ODE were loaded into 3-neck round flask and degassed at 100 °C for 30 min. When the degassing was finished, it was cooled down to room temperature and filled with Ar gas, then 0.1 mmol of (TMS)₃P in 1mL of ODE was injected at an elevated temperature (~150 °C). Next, the mixture was quickly heated up to 300 °C with strong agitation under Ar atmosphere keeping 10 min. After that, 5 mL of Zn(OA)₂ solution, and 0.1 mmol of Se and 1.9 mmol of S dissolved in 2 mL of TOP were sequentially added into the reaction system which was cooled down to 220 °C beforehand,

and then were repeatedly heated up to 300 °C for 20 min. After cleaning, the resulting precipitate was dispersed in toluene. The cadmium-free QDs consisting of InP cores coated with ZnSeS composition gradient shells were obtained. The the energy-dispersive X-ray spectroscopy (EDS) spectrum in Figure 5-1 showed that the presence of In, P, Zn, S and Se elements, which further confirmed that the core-shell structured InP/ZnSeS QDs were formed. The low-magnification transmission electron microscopy (TEM) exhibited that these QDs have a narrow size distribution with a mean diameter of 4-6 nm, as shown in the inset of Figure 5-1.

Figure 5-1. (a) EDS of the resulting InP/ZnSeS QDs. The samples were tested on a quartz substrate (main component:SiO₂). Inset: TEM image of the resulting InP/ZnSeS QDs at low magnification.

The absorption and photoluminescence (PL) spectra of the resulting InP/ZnSeS QDs measured at room temperature were shown in Figure 5-2a. From the PL spectrum, it could be seen that there was no surface defect emission from the resulting QDs, and a strong green emission, consisted of a band edge emission with a peak wavelength of 541 nm and a linewidth of 52

nm was observed (by 400 nm excitation). It is worth mentioning that the core-shell structure of the resulting QDs may lead to dramatically improved emission intensity. As shown in Figure 5-2b, compared with the QDs without ZnSeS shell, the emission intensity of the QDs coated with ZnSeS shell show the more than 2.5-fold enhancement in emission intensity, which corresponds to a high QY level of $\sim 53\%$. It can be noted that the QDs without ZnSeS shell have a zinc-rich surface owing to the addition of Zn(OA)_2 which reduces the amount of surface defects in InP QDs to a certain extent.

Figure 5-2. (a) UV-Vis absorption and PL spectra of the resulting InP/ZnSeS core-shell QDs. (b) PL spectra of the InP QD cores with zinc-rich surface and InP QDs with ZnSeS shell.

5.3.2 Electrical Characterization of Green QLEDs and Device Analysis

The QLED output spectrum was recorded at the bias voltage of 6.5 V. Figure 5-3a shows a clear green emission peaking at 550 nm with a FWHM of 55 nm. The resulting QLED shows a red-shift along with spectral broadening of EL versus PL due to the combination of Förster energy transfer, dielectric dispersion and electric-field-induced Stark effect [6,18,95]. The weak emission in the blue-wavelength region is from poly-TPD. The emission from poly-TPD

can be changed by controlling the hole-transporting layer (poly-TPD) and electron-transporting layer (TPBi) thicknesses in the device. Figure 5-3b presents the output performance of the optimized InP-based QLEDs. Its maximum brightness is close to 700 cd/m^2 and the external quantum efficiency (EQE) is 0.26 %, which are significantly improved compared to the previously reported values (i.e., the maximum brightness and EQE were around 16 cd/m^2 and 0.008 %, respectively). The inset of Figure 5-3b shows the structure of these QLEDs tested.

Figure 5-3. (a) EL spectrum and (b) current density-voltage and luminance-voltage characteristics of the resulting QLED. Inset: the structure of the InP-based QLEDs.

A QD-free LED processing with the structure of ITO/PEDOT:PSS/poly-TPD/TPBi/LiF/Al was also fabricated for comparison. Interestingly, we observed that, besides the blue poly-TPD emission, a strong red emission peaking at ~ 620 nm appeared (Figure 5-4). In addition, the red emission shows a strong voltage-dependence. At low bias (5 V), the EL spectrum is clearly dominated by emission from the poly-TPD due to most of the excitons are formed inside the bulk of the poly-TPD and there is no red emission observed. As the applied voltage is increased, the recombination region of excitons shifts toward the interface of poly-TPD and TPBi, where the red emission occurred and its relative contribution enhances compared with the blue emission of poly-TPD. The process is discussed in more detail below.

Figure 5-4. EL spectra of the device without QDs for different applied biases.

This red emission is attributed to an exciplex formed at the interface between poly-TPD and TPBi. Such exciplex is a kind of excited state complex formed between the donor and the acceptor, which are in the excited state and the other in the ground state respectively. A similar exciplex emission formed

between hole-transporting layer and polyfluorenes is previously reported by Li *et al* [152]. For our case, from the energy levels of poly-TPD and TPBi shown in Figure 5-5, it can be found that the energy gap between the HOMO of poly-TPD (~ 5.2 eV) and the LUMO of TPBi (-3.2 eV) is ~ 2.0 eV, which is perfectly matching the red emission band. Such red emission from charge-transfer (CT) exciplexes formed at the interface between poly-TPD and TPBi can be utilized for white QLEDs.

Figure 5-5. Energy band diagram of the devices without QDs.

To combine the green (QDs), blue (poly-TPD), red (exciplex) emission for a white LED, we fabricated the QLED with loosely packed QD film where there are some space between the adjacent QDs to facilitate a direct contact of poly-TPD and TPBi (Figure 5-6a). The loosely packed QD layer was obtained by reducing the concentration of QDs and increasing the speed rate of spin-coating. Figure 5-6b shows the atomic force microscope (AFM) images of loosely packed QD layer deposited onto a 40 nm thick poly-TPD layer annealed at 110 °C, and voids between QDs can be clearly observed in the corresponding inset of Figure 5-6b.

5.3.3 Realization of Ternary Complementary White QLEDs

Figure 5-6. (a) Schematic illustration of ternary complementary QLED (not drawn to scale). A loosely packed layer of quantum dots located at the interface between poly-TPD and TPBi with QDs embedded into electron transporting (TPBi) films. (b) AFM topography (height) image of a loosely-packed QD film spin-coated on top of poly-TPD.

The QLED output spectrum recorded at the bias voltage of 15 V exhibits a broadband coverage over the entire visible wavelength range, and main emission peaks can be observed in the spectrum (Figure 5-7a). The green emission of QDs is spectrally complementary to the blue emission from poly-TPD and the red emission from the exciplex of poly-TPD and TPBi for white light generation. The CIE coordinates of the InP-based QLED is (0.349, 0.342), which is close to the balanced white coordinates (Figure 5-7b). In addition, the

white light of the QLED is characterized with a high CRI of 95 and a moderate CCT of 4710 K. The CRI is significantly higher than that of most of solid-state white LEDs. An image of the white QLED output was recorded at a luminance of 322 cd/m^2 (inset of Figure 5-7b), which displays bright and uniform white emission.

Figure 5-7. (a) EL spectrum of ternary complementary QLEDs. (b) CIE chromaticity coordinate diagram of the white QLEDs, along with a photograph of a QLED with a pixel size of $3 \text{ mm} \times 3 \text{ mm}$ (inset).

The spectral power distribution of the ternary complementary QLEDs presented herein also exhibits distinctive voltage dependence. Figure 5-8a shows the EL spectrum colour shift in the QLED at the low applied bias (12 V) and high applied bias (16 V). With increasing bias, we observed a rapid increase of the red spectral component in the EL spectrum relative to the initially dominant blue and green spectral components. This evolution of spectral features with the increasing bias was consistent with that of the devices without QDs (Figure 5-4). It can be seen that the blue spectral component from poly-TPD enhances relatively faster with the increasing bias compared with the

green emission from QDs. This indicates that more excitons are harvested in poly-TPD possibly due to the reduced exciton confinement effect of poly-TPD on the QD layer as the driving voltage increases. The colour coordinates for the QLEDs under different bias conditions (12-16 V) have been calculated in the present study and presented in the CIE 1931 colour diagram in Figure 5-8b. The chromaticity calculation suggests that it is possible to tune the desired colour coordinates of the three emissive complements in the QLED by adjusting the bias voltage.

Figure 5-8. (a) EL spectra of the resulting QLED under low voltage (12 V) and high voltage (16 V), and (b) CIE chromaticity coordinate diagram for the QLED at different biases.

5.4 Conclusion

In conclusion, the InP-based QLEDs with efficient green emission have been fabricated in the work. Additionally, with the design of a loosely packed QD layer resulting in the partially direct contact of poly-TPD and TPBi, a ternary complementary white QLED consisting of blue component (poly-TPD),

green component (QDs) and red component (exciplex formed at the interface between poly-TPD and TPBi) has been demonstrated with a high colour rendering index of 95. Realistic progress towards the practical application in white QLEDs using InP-based QDs has been achieved. Furthermore, the successful realization of the ternary complementary white QLEDs may provide a promising strategy for design and fabrication of high-performance optoelectronic devices with tunable multi-colour components.

Chapter 6 Electrically Driven, Flexible, Large-area, Quantum Dot Light Emitting Tapes

6.1 *Introduction*

Quantum dot light emitting diodes (QLEDs), typically using a QD film thickness of less than hundred nanometers, are very thin, making them virtually transparent and flexible, the key elements that OLEDs have been successfully demonstrated for the future information displays [153-156]. However, the challenges remain intact in development of flexible QLEDs due to the specific requirements of electrodes and flexible substrates for device fabrication and operation. Indium tin oxide (ITO) is still the main electrode material for flexible and non-flexible QLEDs [21,157], but its brittle nature [14, 158-160] is not quite suitable for flexible optoelectronic devices. The QLED fabrication involves multiple steps of solution-processed techniques with various chemicals and high temperature annealing, therefore limiting the device architecture designs and the choices of suitable flexible plastic substrates. For example, the aqueous polyethylene dioxythiophene:polystyrene sulfonate (PEDOT:PSS), which is widely used as a buffer layer for QLED fabrication, is generally annealed at ~150 °C, to remove solvents and functionalize this charge injection layer [15,39]. Such high temperature annealing usually causes the destruction or distortion of flexible substrates. In addition, only few types of plastic such as poly(ethylene-terephthalate) (PET) can be used as flexible substrates because the common solvents, e.g., toluene often damages organic substrates. Relaxing these requirements to achieve flexible QLEDs results in greatly limited device performance.

In this section, we report novel flexible top-emitting QLED tapes employing inverted device architecture with Kapton polyimide as the substrate and metallic thin films (Al, Ag) as the electrodes. Highly flexible Kapton polyimide films are stable against many organic solvents and can withstand relatively high temperatures (~ 260 °C), which allowed us to optimize for the best device performance. Such highly flexible top-emitting QLED films demonstrate the maximum brightness and efficiency values of $20,000 \text{ cd m}^{-2}$ and 4.03%, which are the highest performance values for flexible QLEDs reported to date. By controlling the QD emission wavelength during colloidal synthesis, we achieved flexible QLED tapes with very high performance in all three colours: red, green and blue (RGB). As an additional advantage of the Kapton tape (optionally one side with adhesive) and the mechanically robust structure, the resulting QLED films can be easily placed on (and removed from) essentially any three-dimensional surface, even with a very large active area of $2 \text{ cm} \times 2.5 \text{ cm}$, the largest flexible QLED. The uses are akin to QLED stickers. These results demonstrate a new route towards flexible QLEDs for information display applications.

6.2 Experiment Details

6.2.1 Synthesis of Multicoloured QDs and ZnO NPs

Red emitting CdSe/CdS/ZnS core-shell structured QDs, green and blue emitting CdSe/ZnS QDs with chemical-composition gradients were prepared using a one-pot synthesis method [8]. For a typical preparation of green-emitting QDs, 0.1 mmol of cadmium oxide (CdO), 4 mmol of zinc acetate ($\text{Zn}(\text{Acet})_2$), 5 mL of oleic acid (OA) were loaded in a 50 mL 3-neck flask,

heated to 150 °C under vacuum to form cadmium oleate ($\text{Cd}(\text{OA})_2$) and zinc oleate ($\text{Zn}(\text{OA})_2$). Next, 20 mL of 1-octadecene (1-ODE) was added to the reaction flask and the reactor was then filled with nitrogen and heated up to 300 °C. At the elevated temperature, 1.6 mL of tri-n-octylphosphine (TOP) dissolving 0.15 mmol of selenium (Se) and 4 mmol of sulphur (S) was injected into the flask swiftly, and the reaction mixture were maintained at 300 °C for 10 min for the QD growth. To purify the synthesized QDs, the reaction mixture was cooled down to room temperature, and the QDs were extracted by the addition of acetone and methanol, followed by centrifugation. The as-prepared QDs were readily dispersed in toluene.

ZnO nanoparticles with a typical mean diameter of 3-4 nm were synthesized based on a solution-precipitation process [12]. For a typical synthesis, zinc acetate in dimethyl sulfoxide (DMSO) (0.1 M, 30 mL) and tetramethylammonium hydroxide (TMAH) in ethanol (0.55M, 30 mL) were fully mixed and stirred for 1 h in ambient air, and then washed at least 4 times with excess precipitant solvents such as hexane:ethanol (1:4 by volume). Finally, the resulting white precipitant was dispersed in butanol at a concentration of $\sim 25 \text{ mg ml}^{-1}$.

6.2.2 Fabrication of Flexible QLED Devices

The Al cathode (190 nm) was first deposited on Kapton tape. The ZnO nanoparticle layer was then spin-coated on the Al cathode deposited kapton tape from ZnO butanol solution at 500-6000 r.p.m. for 60 s and annealed at 150 °C for 30 min in a nitrogen glove box. Next, the QD film was deposited on the top of ZnO NPs layer by spin-coating the QD dispersion (QDs were

dispersed in toluene with a concentration of 15 mg/mL) at a rate of 1000-6000 r.p.m. for 60 s, and baked at 90 °C for 30 min. After that, the samples were loaded into a high-vacuum deposition chamber (at a based pressure of $\leq 2 \times 10^{-4}$ Pa) to thermally deposit the 2,2',2''-tris-(N-carbazolyl)-triphenylamine (TCTA, 60 nm), MoO₃ (10 nm), and Ag (18 nm) layers.

6.2.3 Characterization

The electroluminescence (EL) spectra of the flexible QLED films were measured using a Photo Research PR705 Spectra Scan spectrometer, while the luminance–current–voltage characteristics of the devices were measured simultaneously with a programmable Yokogawa GS610 source meter and a Konica Minolta luminance meter LS-110 in air at room temperature. Atomic force microscope (Cypher AFM, Asylum Research) was used to characterize the morphology of the ZnO nanoparticle film. The photoluminescence (PL) spectra were recorded using a Shimadzu RF-5301PC spectrofluorophotometer equipped with a 150 W Xenon lamp as the excitation source. All measurements were carried out at room temperature under ambient conditions.

6.3 Results and Discussion

6.3.1 Structure of Top-emitting QLED Tapes

The top-emitting device architecture was demonstrated in inorganic and organic LEDs with advantages of enhanced aperture ratio of display [161]. We first employed this architecture to design the flexible QLED films as the top-emitting LEDs are of increasing interest since the light outcoupling from the top allows LED devices on opaque substrates, which is quite useful for many

applications such as high-resolution active matrix (AM) displays [162,163]. The corresponding structure of the resulting QLED films comprises a multilayer thin film architecture of Kapton tape/Al/ZnO nanoparticles (NPs)/QDs/2,2',2''-tris-(N-carbazolyl)-triphenylamine (TCTA)/MoO₃/Ag, as shown in Figure 6-1a. The thickness of Ag layer (anode) on top of the device was optimized at 18 nm to balance between conductivity and transmissibility for the best device performance. The CdSe/ZnS core-shell structured QDs, prepared by one-pot synthesis method [8], were used as the emissive layer. The ZnO nanoparticle film serving as electron transport layer (ETL) was spin-casted from ZnO nanoparticles in butanol solution. In our work, we achieved uniform ZnO nanoparticle films by the modification of the surface properties of ZnO NPs. The ZnO NPs employed here were prepared with an approach modified from the previously reported by a solution-precipitation process [12]. The surface ligands of the ZnO NPs were removed by adding excess precipitant solvent (hexane/ethanol) and then the resulting white precipitant was dispersed into butanol. As shown in Figure 6-1b, the surface roughness (RMS) of the film made from a ZnO nanoparticle butanol solution is only 3.6 nm, about the size of ZnO nanoparticles, indicating excellent surface smoothness. The schematic energy level diagram of the device depicted in Figure 6-1c shows that the electrons can easily be injected from the Al to the QD layer via conduction band of ZnO nanoparticle layer. However, the case is different for the hole injection [95,108,110]. For n-doped MoO₃, owing to the deep lying electronic states of MoO₃, the hole injection from anode to the organic semiconductor (TCTA) results from carrier breakthrough the MoO₃/TCTA junction. The electrons are extracted from the highest occupied molecular orbital (HOMO)

level of TCTA through the conduction band of MoO₃. Figure 6-1d displays bright, uniform and saturated green QD emission from the resulting flexible QLED film with a surface area of 2 cm × 2.5 cm, which is the largest area reported for flexible QLEDs so far.

Figure 6-1. (a) Schematic of the QLED film configuration (from the bottom to the top): Kapton tape/Al/ZnO NPs/QDs/TCTA/MoO₃/Ag. The CdSe/ZnS QDs and ZnO NPs layers were deposited by spin-casting method, and other layers were deposited by thermal evaporation. (b) AFM image of spin-coated ZnO nanoparticle ETL formed on the Kapton tape/Al surface. (c) Energy level diagram of the QLED film. (d) Photographic image of a large-area QLED tape placed on a flexible plastic substrate (20 mm×25 mm).

It is worth pointing out that although the high-quality ZnO nanoparticle films deposited on ITO have been achieved before, the present case is quite different with the ZnO nanoparticle film on Al. Figure 6-2 show the digital optical microscopic images of the ZnO nanoparticle films deposited on Al electrodes. Because of the obvious distinction in their surface properties such as

surface energy and hydrophobic/hydrophilic nature [164], ZnO nanoparticle films from ZnO nanoparticles dispersed in ethanol, prepared by the solution-precipitation process method, form multiple small cracks and some large broken areas on Al surface as shown in Figure 6-2a. In contrast, the modified ZnO nanoparticle film from ZnO nanoparticles dispersed in butanol after removing excess organic ligands show a quite smooth surface (Figure 6-2b).

Figure 6-2. Digital optical microscopic images of the ZnO nanoparticle films deposited on Al electrodes. (a) Spin-cast film from ZnO nanoparticles dispersed in ethanol obtained from the solution-precipitation process method. (b) Spin-cast film from ZnO nanoparticles dispersed in butanol after removing excess organic ligands.

6.3.2 Performance and Parameter Optimization of Green QLED Tapes

Figure 6-3a presents the EL spectrum of the typical green QLED tapes. The pure QD emission at a peak wavelength of ~ 508 nm with a full width at half maximum (FWHM) of 34 nm illustrates the highly efficient recombination of electrons and holes in the QD emissive layer. The peak wavelength is red-shifted (~ 6 nm) from the QD solution's photoluminescence (PL) resulting from a combination of finite dot-to-dot interaction in close packed solid films and the electric-field-induced Stark effect. The typical current density and luminance curves as a function of applied voltage for the unpackaged QLED films are shown in Figure 6-3b. The maximum luminance reaches $12,300 \text{ cd/m}^2$ and the turn-on voltage (V_T) of 3.5 V is relatively low, suggesting a small barrier height for the charge injection into the QDs. In addition, the external quantum efficiency – current efficiency – current density (EQE-CE-J) characteristics of the QLED film exhibit high device efficiency, with a maximum EQE of 2.44 % and CE of 6.61 cd/A (Figure 6-3c). The ZnO nanoparticles as ETLs in the inverted QLEDs help neutralizing QDs, i.e., turning dark (charged) QDs to bright (neutral) QDs and, therefore improve the device performance [6]. But as other metal oxides, ZnO also quenches the quantum yield of QDs due to ultrafast non-radiative process that depends on proximity of emitters to the interface. The two opposite effects imply that the device performance is strongly dependent on the thickness of the QD and ZnO nanoparticle layers [12]. Figures 6-3d and 6-3e show the turn-on voltage V_T and maximum EQE as a function of the QD and ZnO nanoparticle layer thickness for the QLED tapes. With the ZnO layer fixed at ~ 38 nm, the lowest V_T of 3.5 V and the maximum EQE of 2.44 % can be achieved when the device is with 19 nm thick QD layer

(Figure 6-3d), which is equivalent to 3 QD monolayers. This result is consistent with the previous reports that few monolayers of QDs are needed for efficient recombination of electrons and holes to provide exciton formation in the QDs [17]. For a 19 nm thick QD layer, increasing the ZnO layer thickness from 20 to 60 nm resulted in a continuous increase of V_T from 3.3 to 5.3 V, while the highest EQE value is achieved when the ZnO thickness is 38 nm (Figure 6-3e). This implies that a finite voltage is needed across the ZnO layer, making the efficiency for the device with a thicker ZnO nanoparticle layer dramatically decreases. In addition to the above factors, we found that the annealing treatment of ZnO nanoparticle film to reduce the defects can also improve the device performance significantly. As shown in Figure 6-3f, for a QLED tape with a 19 nm thick QD layer and a 38 nm thick ZnO nanoparticle layer increasing ZnO annealing temperature from 90 to 180 °C, the V_T shows a steady decrease until 150 °C and the EQE increases to the maximum level of 2.44 % at 150 °C. After that, the EQE and V_T are almost unchanged with increasing annealing temperature. We believe that this is enabled by enhancing the electron transport in ZnO nanoparticle films, which is associated with the reduction in defect concentration of ZnO nanoparticles.

Figure 6-3. (a) Normalized PL and EL spectra for QDs dispersed in toluene and a typical QLED tape at an applied voltage of 6 V, respectively. (b) Current density and peak luminance of the QLED films as a function of bias voltage. (c) External quantum efficiency (EQE) and current efficiency (CE) of the QLED tapes as a function of current density. (d) Turn-on voltage (V_T) and maximum EQE versus QD layer thickness (ZnO nanoparticle layer thickness of 38 nm). The turn-on voltage is defined as the voltage at which the luminance is 1 cd m^{-2} . (e) V_T and maximum EQE vs. ZnO nanoparticle layer thickness (QD layer thickness of 19 nm). (f) V_T and maximum EQE vs. ZnO nanoparticle layer annealing temperature (thickness of QD and ZnO nanoparticle layers is 19 and 38 nm, respectively).

To further confirm the effect of defects in ZnO nanoparticles in the device EL performance, we compared the PL intensity of ZnO nanoparticle

films annealed at different temperatures with an excitation source of 300 nm wavelength. As shown in Figure 6-4, the PL spectra of ZnO nanoparticles consist of a sharp UV emission band and a broad green emission band peaking at 550 nm. The narrow UV emission is attributed to the radiative annihilation of excitons [165], while the broad visible emission is associated with defects in ZnO nanoparticles [166]. The origin of defect emission has been the subject of ongoing debate and the widely accepted theory is that they are caused by the oxygen vacancies or zinc interstitials [167,168]. We observed the PL intensities of the broad green emission band dramatically decrease with the annealing temperature increasing from 90 to 150 °C. Beyond 150 °C, there is no obvious green emission observed from ZnO. In contrast, the UV emission intensities only have small variation, suggesting that the total defect concentration in ZnO is significantly decreased with the increasing annealing temperature. Combining with the observed EQE and V_T trends in the case of QLED films, these results show a good correlation between the device EL performance and defect concentration in ZnO nanoparticles. The significant reduction in the defect concentration and increase in the crystal quality of ZnO nanoparticles improve the electron transport due to the decrease in defect-trapped electrons in ZnO, resulting in the enhanced EL intensity. It should be noted that the annealing temperature of 150 °C is too high for most of flexible substrates, which may limit the QLED device performance to a great extent, while this is fine for Kapton polyimide films.

Figure 6-4. Room temperature PL spectra for ZnO nanoparticle films annealed at different temperatures from 90 and 180 °C.

The thin Ag layer (~18 nm) serves as a semi-transparent anode in our top-emitting QLED tapes, and an organic capping (OC) layer on top of Ag layer could modify the device's optical structure [169]. The OC layer has been demonstrated to improve the outcoupling efficiency of the top-emitting OLED [170]. Here, we deposited a tris-8-hydroxyquinoline aluminum (Alq_3) film as a capping layer above the top contact. Figure 6-5 shows the performance of the device with the OC layer as measured in the vertical direction. We improved the device performance significantly just by adding the optical outcoupling Alq_3 layer with a film thickness of 40 nm. The maximum brightness reaches 20,000 cd/m^2 (Figure 6-5a), and an EQE level of 4.03% and a current efficiency value of 10.9 cd/A can be achieved at a current density of 26.6 mA/cm^2 (Figure 6-5b). The thin OC layer improves the efficiency and the brightness of the resulting flexible QLED film by 165% and 162%, respectively.

Figure 6-5. (a) Current density and luminance of QLED tape as a function of applied voltage. (b) External quantum efficiency and current efficiency of QLED tape as a function of current density.

6.3.3 Electrical Properties of Multi-colour QLED Tapes

Using the optimized structure with multicoloured quantum dots, we performed the RGB-emitting QLED tapes. Figure 6-6a presents the normalized EL spectra of these QLED films with three different peak emission wavelengths (470, 551, and 630 nm) at the applied voltage of 6 V. It can be observed that all the EL spectra are saturated with QD emission and are slightly redshifted (5–6

nm) from the corresponding PL spectra of QD solutions. The FWHM is 33, 37 and 37 nm for the respective RGB colours. The inset shows photographic images of the three operating devices, which display nearly saturated colour emission. As shown by the Commission Internationale de Eclairage (CIE) chromaticity diagram in Figure 6-6b, these QLED films cover a larger area than the high-definition television (HDTV) standard colour triangle [17].

Figure 6-6. (a) Normalized EL spectra of QLED films with peak emission wavelengths of 470 nm (blue), 551 nm (yellowish green) and 630 nm (red). Inset: the photographic images of the RGB QLED tapes. (b) CIE coordinates of the three devices together with the HDTV colour standards.

The luminance and EQE as a function of the current density for the optimized QLED films are shown in Figures 6-7a and 6-7b. The maximum luminance and EQE values of 2,600 cd m^{-2} and 1.40% for the blue emission (peak at 470 nm), 15, 600 cd m^{-2} and 3.09% for the yellowish green emission (at 551 nm), and 8,200 cd m^{-2} and 3.46% for the red emission (at 630 nm) were achieved, respectively. Table 6-1 summarizes the detailed performance parameters of the resulting RGB QLED tapes. The maximum luminance and efficiency are the highest values reported to date for correspondingly coloured flexible QLEDs. Nevertheless, it still can be expected that the further optimization such as improving the quantum yields of QD films would realize better device performances.

Figure 6-7. (a) Luminance of the resulting RGB QLED films as a function of applied voltage. (b) EQE of QLED tapes as a function of current density.

Table 6-1. Summary of the optical and electrical properties of QDs and QLED tapes.

Colour of QLED	PL λ_{max} (nm)	EL λ_{max} (nm)	FWHM (nm)	V_T (V)	EQE _{max} (%)	L_{max} (cd/m ²)	CIE index (x, y)
Blue	465 nm	470	37	3.9	1.40	2,600	0.135, 0.103
Green	502 nm	508	34	3	4.03	20,000	0.086, 0.643
Yellowish green	545 nm	551	37	2.5	3.09	15,600	0.335, 0.631
Red	624 nm	630	33	2	3.46	8,200	0.682, 0.315

6.3.4 Mechanical Properties of QLED Tapes

In addition to the opto-electrically high performance, the distinct advantages of our top-emitting QLED tapes over previous flexible QLEDs are their highly flexible and mechanically robust structure. With the use of Kapton tape, the resulting QLED stickers are easily placed on or removed from any essentially three-dimensional surface, which facilitates the versatile use of our QLED platform. As shown from Figure 6-8a to Figure 6-8d, the green-emitting QLED tape, stuck on a mascot, is working very well with high brightness under room light or dark condition. Furthermore, the operating QLED film can be bent arbitrarily and is free of cracks and dark spots even under almost completely folded bending. As shown in Figures 6-8e and 6-8f, the working QLED tape is placed and bent around a very thin steel plate. Its brightness and uniformity do not show any degradation. The excellent mechanical robustness of the resulting QLED tapes allows us to use as light emitting stickers, i.e., luminescent post-it for three-dimensional surfaces.

Figure 6-8. Photographic images of a QLED tape with a pixel size of 3 mm×3 mm placed on different non-planar surfaces. (a-b) “Off” and “On” device placed on a mascot in a bright room, respectively. (c-d) “Off” and “On” device placed on the mascot in a dark room, respectively. (e-f) “Off” and “On” device placed on a thin steel plate under room light, respectively.

The mechanical robustness of QLED tapes is further investigated by measuring the device brightness after accumulated bending. The device is tested with a configuration where the QLED film is attached onto the surface of cylindrical tubes. The bending diameter is determined by the diameter of the tubes. These flexible QLED films tapes operated at 6 V were repeatedly bent 500 times. Figure 6-9 shows the initial and after-bending brightness characteristic of devices with the different bending diameters of 12, 9 and 4 mm. It can be observed that the tested QLED films are operating very well and there

is no serious deterioration in the EL intensity after repeated bending under ambient conditions. Additionally, it should be noted that the performance degradation would become faster with the decreasing bending diameter. For example, at a bending diameter of 12 mm, the brightness remains 96.5% after 500 bending cycles. However, for a small bending diameter of 4 mm, the brightness remains 87.5% under the same testing condition. The thin semi-transparent Ag anode as opposed to the brittle transparent ITO electrode is the key to successfully demonstrating not only highly flexible but also highly robust QLED platforms.

Figure 6-9. Luminance of the resulting QLED tape at the bias of 6 V as a function of bending cycle number.

6.4 Conclusion

In conclusion, we have demonstrated highly flexible, large-area, full-colour, top-emitting QLED tapes with record high efficiency in flexible QLEDs. These superior performances were achieved by the efficient design of top emitting device architecture with the proper choice of Kapton tape as the

flexible substrate, the surface modification of ZnO nanoparticles for an efficient electron transporting layer, and the deposition of Alq₃ capping layer as an outcoupling element. These large-area, ITO-free QLED films also show excellent mechanical robustness and can be used as electrically driven light emitting stickers on any three-dimensional surface, which enables the extensive and versatile use of LEDs. Our results illustrate a further step towards the practical application of flexible QLEDs in optoelectronic devices including flexible, full-colour information displays and surface lighting.

Chapter 7 Conclusion and Future Works

7.1 Conclusion

Quantum dot-based light emitting diodes (QLEDs) with advantages in colour quality, stability and cost-effectiveness are emerging as a candidate for single-material, full colour light sources. In this dissertation, the performances for the conventional QLEDs are significantly improved in terms of the efficiency, stability, toxicity and flexibility of device. We believe that the results from this dissertation will be valuable in both fundamental and applied research in this field.

For improving device efficiency, we demonstrated, for the first time, the dramatically enhanced light extraction in QLEDs based on a layer of large-scale, periodic ZnO nanopillar arrays fabricated by a simple and efficient PRINT method. The resulting QLED with ZnO nanopillar array pitch of 600 nm showed a record current efficiency (CE) of 26.6 cd/A, and the maximum external quantum efficiency (EQE) of 9.35% achieved in the present work is also the highest EQE value reported for green QLEDs to date, which corresponds to 51.3% efficiency enhancement in total light output compared with the reference device. Two-dimensional finite difference time domain (FDTD) simulations reveal that the significant light out-coupling efficiency improvement is attributed to the effective diffraction of light trapped in the glass mode due to the presence of ZnO nanopillar arrays and the microcavity effects in the inverted QLEDs.

For resolving the toxicity of Cd-based QDs, high-quality InP/ZnS core-shell QDs with luminescence tunable over the entire visible spectrum have been

prepared by a facile one-pot solvothermal method. The excellent optical properties of the resulting QDs including high quantum yields, narrow emission linewidth and good photostability were obtained by effectively passivating the surface defects of InP QD cores with a strain-relieved ZnS shell. The full width at half maximum (FWHM) of the QDs can be as narrow as 38 nm. Furthermore, in this work, a white QLED based on the resulting QDs has been successfully demonstrated with a high colour rendering index of 91. The high performance of the resulting InP/ZnS QDs coupled with their low intrinsic toxicity may further enable industrial applications of these QD emitters.

Additionally, with the design of a loosely packed QD layer resulting in the direct contact of poly-TPD and TPBi, a ternary complementary white QLED consisting of blue component (poly-TPD), green component (QDs) and red component (exciplex formed at the interface between poly-TPD and TPBi) has been demonstrated with an excellent CRI of 95. Realistic progress towards the practical application in white QLEDs using InP-based QDs has been achieved. Also, the successful realization of the ternary complementary white QLEDs may provide a promising strategy for design and fabrication of high-performance optoelectronic devices with tunable multi-colour components.

For developing low-cost, stable QLEDs, we first demonstrated an efficient QLED using solution-processed WO₃ nanoparticle (NP) film as hole injection layer (HIL). Compared with the present PEDOT:PSS-based QLEDs, the resulting WO₃ NP-based QLEDs show obviously enhanced electroluminescence (EL) performance. The EQE of 3.32 % reported in this work is higher than the previously reported values for green emitting QLEDs with a non-inverted structure, and the luminance of 30,006 cd/m² matches that

of the best QLEDs with organics as HTLs/HILs. Besides, the resulting WO₃ NP-based devices exhibit an obvious improvement in the device stability and the operating lifetime is increased by approximately two folds. Furthermore, the solution-processed preparation method of WO₃ NP film used in our work can be suitable for the application in flexible optoelectronic devices due to the low annealing treatment temperature (annealing temperature can be as low as 80 °C). To further improve the device stability, all solution-processed, bright, and stable QLEDs with double-sided metal-oxide (MO) NPs as CTLs (WO₃ NPs and ZnO NPs as the HTL and the ETL, respectively) have been successfully fabricated. The resulting QLEDs show good device performance, with a peak luminance of 21,300 cd m⁻², the maximum CE of 4.4 cd A⁻¹, a low turn-on voltage of 3 V, and a long operating lifetime. The lifetime of the QLEDs with double-sided MO NPs can be almost 20 folds higher than that of the standard device. These results indicate that the solution-processed WO₃ and ZnO NPs can serve as excellent HTL and ETL thin films and offer a practical platform for the realization of low-cost and high-performance active matrix-driven QD displays.

For the study on flexible QLEDs, we have demonstrated extremely efficient, highly flexible, large-area, full-colour, top-emitting QLED tapes, where the maximum luminance and EQE values of 2,600 cd m⁻² and 1.40 % for the blue emission (peak at 470 nm), 20,000 cd m⁻² and 4.03 % for the green emission (at 508 nm), and 8,200 cd m⁻² and 3.46 % for the red emission (at 630 nm). These superior device performance can be primarily attributed to the efficient design of device architecture, such as the use of Kapton tape as the flexible substrate (withstanding high annealing treatment and stable against

organic solvents), the modification of ZnO nanoparticle solution (forming uniform film on Al electrode), the deposition of Alq₃ capping layer (reducing the microcavity effects), etc. Meanwhile, these ITO-free QLED tapes also show excellent mechanical robustness and facile use capability that they are easily stuck on three-dimensional surfaces, which facilitates the extensive and versatile use of LEDs. The approach reported here represent a further step towards the practical application of flexible QLEDs, and open the door to simple and high quality nanocrystal-based flexible light sources in optoelectronic devices such as flexible, full-colour displays and solid-state lighting.

7.2 Future Works

Nowadays, the performance of QLEDs still falls short of meeting the technical requirements needed for practical applications. The EQEs in most of QLEDs are only a few percent (less than 10%), and need to be further improved. Therefore, we should focus on the research on the improvement for the efficiency of QLEDs in the future. The detailed plan is discussed below.

7.2.1 Preparation of QDs with Organic/Inorganic Hybrid Ligands and Their Application in QLEDs

The high efficiency of QLEDs can be attributed to the concomitant excitation of the luminescent QD film via Förster energy transfer and direct charge injection. This requires facile transport of charge carriers to QDs. The efficiency of moving charges to QDs is strongly dependent on the QD environment. The surface of QDs prepared by traditional colloidal techniques is

capped with an insulating layer of organic ligands with long hydrocarbon tails [10]. As a result, the benefits of quantum-confined materials are outweighed by inefficient injection.

The important breakthrough in improving the electron mobility of QD layer is associated with the works of the Talapin's group [171-174], who successfully realized that the inorganic ligands connected QDs by ligand exchange method. It can be reasonably assumed the device performance would be improved if the hybrid-ligand QDs with enhanced electron mobility are used in the QLEDs. In our proposed work, we design an organic-inorganic hybrid ligand prepared by introducing inorganic ligands such as S^{2-} , HS^- , Se^{2-} , HSe^- , Te^{2-} , HTe^- , TeS_3^{2-} , OH^- , and NH_2^- into organic ligands of QDs using the reported ion-exchange method, resulting in the enhanced electron mobility in QDs. We believe the organic-inorganic hybrid ligands would favour charge injection into QDs greatly and the stability of QLEDs will be also improved due to the inorganic ligands are stable as compared to organic ligands.

7.2.2 Improving Device Efficiency of QLEDs by Localized Surface Plasmon Resonance

Localized surface plasmon resonance (LSPR) is a long studied nanoscale phenomenon with considerable recent interest [175-182]. The past decade has witnessed significant improvements in the applications for biosensors, OLEDs and solar cells. For example, recently Xiao *et al.* [179] demonstrated the surface plasmon-enhanced electroluminescence in OLEDs by incorporating Au NPs in the hole injection layer of PEDOT:PSS. An increase of ~25% in the EL and efficiency are achieved for these devices with Au NPs.

We intend to adopt a standard QLED structure with a multilayer thin film architecture of ITO/PEDOT:PSS/poly-TPD/QDs/TPBi/LiF/Al to study the surface plasmon-enhanced electroluminescence in QLEDs. In this work, the Au nanoparticles and PEDOT:PSS can be firstly mixed well by using water-soluble Au nanoparticles and PEDOT:PSS because of the same solvent used. Note that the emission spectrum of QDs is required to match with the absorption of Au nanoparticles. Poly-TPD used here not only acts as a hole transport layer but also as a spacer for adjusting the distance between QDs and mixture layer to avoid the fluorescence quenching due to their extraordinary high molar extinction coefficients and broad energy bandwidth of metals. An enhanced EL emission can be expected from the proposed QLEDs due to the surface plasmon coupling of Au NPs when the spectral overlap between the absorption of Au NPs and QDs EL matches well. In the proposed work, the effects of the spacer thickness and the concentration of Au NPs in PEDOT:PSS on QLED performance will be studied in detail.

List of Publications

Journal Paper

1. **X. Yang**, D. Zhao, K. S. Leck, S. T. Tan, Y. X. Tang, J. Zhao, H. V. Demir, and X. W. Sun, "Full visible range covering InP/ZnS nanocrystals with high photometric performance and their application to white quantum dot light-emitting diodes," *Adv. Mater.* vol. 24, pp. 4180–4185, 2012.
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9. **X. Yang**, E. Mutlugun, C. Dang, K. Dev, Y. Gao, S. T. Tan, X. W. Sun, and H. V. Demir, “Highly flexible, electrically driven, top-emitting, quantum dot light-emitting stickers,” *ACS Nano*, in press, 2014.
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Conference Paper

14. **X. Yang**, S. T. Tan, H. V. Demir, and X. W. Sun, “High-quality InP/ZnS nanocrystals with high photometric performance and their application to white quantum dot light-emitting diodes,” *IEEE Photonics Conference (IPC)*, pp. 758–759, 2012.
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Layer”, *ICMAT*, Material Research Society (MRS) Singapore, June 30 – July 5, 2013.

Award

- Best Student Paper Award (Third Place), IEEE Photonics Conference 2013, USA, September 2013.
- Chinese Government Award for Outstanding Self-financed Students Abroad, China, March 2014.

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