Device optimization for high-performance quantum dot-based light-emitting diodes

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DEVICE OPTIMIZATION FOR HIGH- PERFORMANCE QUANTUM DOT- BASED LIGHT-EMITTING DIODES

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Abstract

Recent two decades have witnessed the burgeoning development of quantum dot-based light-emitting diodes (QLEDs) since its first demonstration in 1994. It has been regarded as one of the next-generation lighting and display technologies, mainly due to the confirmed extraordinary advantages such as tunable wavelength across the whole visible spectrum, narrow full-width at half-maximum (FWHM), superior color saturation feature and economical manufacture accessibility. Although tremendous achievements in this research area have been attained especially in recent two to three years, which have proved its comparable performance with organic LEDs (OLEDs), there still remain some deficiencies yet to be overcome. This thesis will focus on the following topics regarding to the manipulation of carrier injection balance, the replacement of charge injection layers and the realization of full-inorganic prototype QLEDs.

First of all, a novel cathode interfacial material (CIM) was introduced to improve the QLED performance by modulating the charge balance. With its promising electron transport behavior and low processing temperature, the resultant devices demonstrate better features in terms of external quantum efficiency (EQE), current (CE) and power efficiencies (PE). Furthermore, by incorporating this CIM with traditional LiF together as the cathode buffering layers, the corresponding device showed superior performance, which could be attributed to the better energy band alignment and more balanced charge injection due to the reduced barrier for electron injection from cathode.

Meanwhile, two inorganic materials, sol-gel prepared copper oxide (CuO) and commercially-available copper thiocyanate (CuSCN) were utilized as the replacements for poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), respectively. For CuO-based QLED, the operation lifetime is

enhanced due to the introduction of inorganic hole injection material, while the device performance is comparable with PEDOT:PSS-based ones. Furthermore, an inorganic CuSCN with simpler preparation method was applied, and the turn-on voltage of the corresponding QLED was dramatically decreased due to the better energy band alignment of CuSCN than PEDOT:PSS with comparable device performance.

Moreover, in order to further promote the stability of QLEDs, devices using inorganic materials with optimization were proposed with specific design philosophy. By the insertion of thin lithium fluoride (LiF) as the insulating as well as buffering layer, the QD charging and carrier imbalance were suppressed in the operating device, resulting in improved performance with an external quantum efficiency of 1.74% and a maximum brightness over 7,600 cd/m², which are among the best reported values for all-inorganic QLED to the best of our knowledge.

To sum up, this thesis mainly addresses three aspects of the current deficiencies in QLEDs. First, a surpassing charge balance was achieved by the manipulation of cathode buffering layers, demonstrating the feasibility of the CIM in improving the device performance. On the other hand, two alternative inorganic materials have been introduced as the hole injection material for substituting PEDOT:PSS, resulting in improved device operation lifetime and lower turn-on voltage; Furthermore, all-inorganic QLEDs with record performance so far were systematically fabricated with proper device engineering. We firmly believe that the aforementioned demonstrated results enable new guidelines and prospects for the development and growth of QLED community.

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List of Abbreviations

1-ODE	1-octadecene
AFM	Atomic force microscopy
Alq ₃	Tris-8-hydroxyquinoline
	aluminium
CB	Conduction band
CBP	4,4'-Bis(N-carbazolyl)-1,1'-biphenyl
CdO	Cadmium oxide
CdS	Cadmium sulphide
CdSe	Cadmium selenide
CE	Current efficiency
CIE	Commission Internationale de l'Eclairage
CIM	Cathode interfacial material
CRI	Colour rendering index
Cs(OA) ₂	Cesium oleate
Cs ₂ CO ₃	Cesium carbonate
CTL	Charge transport layer
CuO	Copper oxide
CuSCN	Copper (I) thiocyanate
DES	Diethyl sulphide
DI-water	De-ionized water
DMSO	Dimethyl sulfoxide
EDS	Energy-dispersive spectroscopy
EL	Electroluminescence
EPD	Electrophoretic deposition
EQE	External quantum efficiencies
ETL	Electron transport layer
FE-SEM	Field-emission scanning electron microscopy
FPD	Flat-panel displays
FWHM	Full-width half-maximum
HDTV	High-definition television
HIL	Hole injection layer
HOMO	Highest occupied molecular orbital
HTL	Hole transport layer
IEA	International energy agency
InP	Indium phosphide
IPA	Isopropyl alcohol
ITO	Indium tin oxide

LE	Luminous efficiency
LED	Light-emitting diode
LiF	Lithium fluoride
MEA	Monoethanolamine
MoO ₃	Molybdenum oxide
NiO	Nickel oxide
NIR	Near infrared
NP	Nanoparticles
OA	Oleic acid
OLA	Oleylamine
OLED	Organic light-emitting diode
OPV	Organic photovoltaic
PCE	Power conversion efficiency
PDMS	Poly(dimethylsiloxane)
PE	Power efficiency
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene)- poly(styrenesulfonate)
Phen-NaDPO	1,10-phenanthroline-(2- naphthyl)diphenyl-phosphine oxide
PL	Photoluminescence
PMMA	Poly(methyl methacrylate)
poly-TPD	Poly(N,N'-bis(4-butylphenyl)- N,N'-bis(phenyl)benzidine)
PPV	P-paraphenylene vinylene
PVK	Poly(9-vinylcarbazole)
QD	Quantum dot
QLED	Quantum dot-based light-emitting diode
QY	Quantum yield
RF	Radiofrequency
RMS	Root mean square
RPM	Round per minute
Se	Selenium
TADF	Thermally activated-delayed- fluorescence
TEM	Transmission electron microscopy
TFB	Poly[(9,9-dioctylfluorenyl-2,7- diyl)-co-(4,4'-(N-(4-sec- butylphenyl)diphenylamine)]
T _g	Glass transition temperature
TMAH	Tetramethylammonium hydroxide
TOP	Trioctylphosphine

TPBi	2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)
TPD	N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine
UPS	Ultraviolet photoelectron spectroscopy
V ₂ O ₅	Vanadium oxide
VBM	Valence band maximum
WF	Workfunction
WO ₃	Tungsten oxide
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
Zn(Ac) ₂	Zinc acetate
ZnO	Zinc oxide
ZnS	Zinc sulphide

Chapter 1 Introduction

1.1 Background

It has been widely recognized that since Thomas Edison improved the practical incandescent lamp as well as proposing its commercialization in the nineteenth century^{1, 2}, artificial lighting has become the most common but indispensable technology in the modern society. The all humanity has witnessed a brand-new world with a fast-developing industry and a rapidly-growing standard of living in the last two centuries. Nowadays, as the economy and population of the world increases sharply, so does the extensive application of the artificial lighting. It has been reported that nearly twenty percent of the world's electricity is consumed for lighting in both residential and commercial sectors every year^{3, 4}. According to the recent publication by International Energy Agency (IEA), the yearly world electricity consumption has a value of 20,900 TWh, which means that nearly 4,000 TWh of energy is used for lighting application^{3, 5, 6}. Such a number equals to a consumption of nearly two billion tons of coal, forty billion Mcf (1,000 cubic feet) of natural gas or seven billion barrel of petroleum. What's more, the traditional fossil fuel resources which occupy an 86.4% share in primary energy consumption are non-renewable and becoming more and more scarce^{7, 8}. All these data and stark reality alerts us to explore alternative renewable resources and further improve the energy efficiency by developing better devices with lower power consumption and better performance.

Light-emitting diodes (LEDs) aiming for solid-state lightings as well as displays have emerged as alternative and promising technologies with superior luminance and higher efficiency compared with conventional fluorescent lamps⁹. Theoretically, a light-emitting diode is a simple p-n junction semiconductor diodes emitting light when being applied by a suitable positive voltage to its two

electrodes¹⁰. In the effective area, electrons are capable to recombine with holes within the device by releasing energy in the form of photons. The wavelength of the emitting wavelength depends on the bandgap of the semiconductors. Although the early demonstration of LED was an infrared one with low intensity¹¹, it has been proved later that LEDs have lots of advantages over conventional incandescent light source such as smaller size, higher luminescence, lower power consumption, etc. Later, in 1962, the first visible LED was developed by Nick Holonyak, Jr. from General Electric Company¹². This device has a $\text{GaAs}_{1-x}\text{P}_x$ p-n junctions, emitting light with a center wavelength of 710 nm.

It is obvious that, in order to use LEDs for lighting purpose, the emission spectrum must cover the whole visible range¹³. The invention of efficient GaN-based LEDs makes it possible. In 1990s, Shuji Nakamura developed the first nitride-based blue/green LEDs, leading to a revolution in the field of GaN-based solid-state lighting and displays^{14, 15}. Therefore, the Nobel Prize in Physics of 2014 was awarded to Shuji Nakamura and other two Japanese scientists “for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources”¹⁶.

The 21st century has witnessed the development and commercialization of III-V based LEDs for solid-state lighting and displays with numerous of products on the markets^{15, 17-19}. But researchers have been still exploring more. Quantum dot-based light-emitting diodes (QLEDs), on the other hand, are considered as the next generation display technology²⁰. Thanks to the narrow emission linewidth²¹⁻²⁶, tunable emission wavelength over the whole visible range²⁷⁻³⁴ and low-cost fabrication techniques^{33, 35-39}, QLEDs already prove themselves to be qualified candidates for next-generation solid-state lighting and display applications. The first demonstration of QLEDs was presented by V.L. Colvin et al. from UC Berkeley, reporting a cadmium selenide (CdSe) QD-based hybrid

inorganic/organic electroluminescence device. Although the device has both emissions from CdSe and p-paraphenylene vinylene (PPV) and an external quantum efficiency lower than 0.01%, this work definitely shed light on the bright future of this research field and its promising business prospects⁴⁰.

Through two decades' efforts made by dedicated researchers and scientists all over the world, currently, the overall performance of QLEDs are reaching a level which is almost comparable with the-state-of-the-art commercial OLEDs regarding color saturation, color purity and color rendering index (CRI)^{25, 41, 42}. Currently, the highest external quantum efficiencies (EQE) of red, green and blue (RGB) QLEDs are 20.5, 14.5 and 12.2%, respectively, all with inorganic-organic hybrid structures⁴¹⁻⁴³. We have to notice that the EQE of 20.5% is arriving the theoretical maximum EQE of such structure configuration⁴⁴. Meanwhile, the maximum luminance of red, green and blue QLEDs are with numbers of 52,000, 218,000 and 7,600 cd/m², respectively^{25, 31, 43}. Therefore, QD-based technology has already been commercialized by several companies such as Color IQ, Amazon, TCL and Samsung in the past few years, as exemplified in Figure 1-1⁴⁵⁻⁴⁹.

Figure 1-1. (a) Photographs of full-color QD solutions from Color IQ. (b) Amazon's Kindle Fire HDX. (c) Quantum dot displays from TCL and Nanosys. (d) Samsung SUHD TV based on quantum dot technology.⁵⁰⁻⁵³

1.2 Basic device structure of quantum dot-based LEDs

In order to introduce the structure configuration of QLEDs, we shall first brief the structure of organic LEDs (OLEDs) because of the fact that QLEDs borrow a lot from the latter in both the fabrication expertise and mechanism explanations⁴⁴. The first organic electroluminescence device was reported by Prof C. W. Tang from Kodak in 1987, where a double-side structure was applied to emit green light from organic thin films, as shown in Figure 1-2^{54, 55}. Later, R. H. Friend's group from Cavendish Laboratory published conjugated polymer-based LED with a quantum efficiency up to 0.05%⁵⁶. Since then, OLED has entered the new era with fast-improved performance and more complicated structure design⁵⁷. From its primitive two-layer structure where the organic layer acts as both emitting layer and hole transport layer (HTL) while another layer plays a role in transporting electrons, more advanced OLEDs normally have

structures with three or more layers including the HTL, emitting layer and electron transport layer (ETL). Such configuration has been applied by researchers in developing QLEDs with high efficiency.^{58, 59}

Figure 1-2. (a) Device configuration and (b) electroluminescence spectrum of OLED.⁵⁴

In a typical QLED structure, the quantum dots (such as CdSe, CdSe/ZnS core-shell, InP, CuInS, or silicon nanocrystals^{26, 40, 44, 60-63}) can serve as the active layers, sandwiched by the HTL and ETL, respectively, as shown in Figure 1-3(b) while the structure of OLED in Figure 1-3(a) for comparison^{64, 65}. HTL and ETL are known as charge transport layers (CTL) for efficient injection of holes and electrons into QDs to generate photons. Therefore the emission wavelength of the device solely depends on the emission spectrum of QDs, which means that QLEDs can emit lights covering the whole visible spectrum from deep-blue to red by simply changing the size and compositions of the materials, as shown in Figure 1-4.

Figure 1-3. Schematic diagram of typical configurations of (a) OLED and (b) normal structure QLED, respectively.

Figure 1-4. Photograph of QDs with different composition and varying size, showing corresponding photoluminescence under UV excitation.

1.3 Parameters and setups for evaluating quantum dot-based LEDs

Given the extreme similarity in both the device configuration and fabrication techniques, the concepts and equipment which has been widely accepted, developed and applied in OLEDs fabrication and characterization can likewise be transplanted to the evaluation of QLEDs with minor modifications. First of all, there are some definitions which should be introduced.

1.3.1 Performance parameters

Internal Quantum Efficiency (η_{int}). Because of the existence of defects and other nonradiative pathways, photo-induced or electrical-injected carriers in QDs can recombine via both radiative and non-radiative pathways. Therefore, parts of the injected electron-hole pairs will recombine non-radiatively instead of radiatively generating lights⁵⁹. The definition of internal quantum efficiency (η_{int}) is as follows:

$$\eta_{int} = \frac{(\text{number of photons generated per second})}{(\text{number of electrons injected into LED per second})} = \frac{P_{int}/h\nu}{I/e} \quad (1-1)$$

Where P_{int} is the optical power of the emitting area, and I is the injected current of the device.⁵⁹

Light Extraction Efficiency ($\eta_{extraction}$). Theoretically, the photons generated by electron-hole recombination should emit into free space. However, not all the photons will be coupled out of the device due to internal reflections and/or reabsorption effects⁴⁴. Therefore, the definition of light extraction efficiency ($\eta_{extraction}$) is therefore presented as:

$$\eta_{extraction} = \frac{(\# \text{ of emitted photons})}{(\# \text{ of generated photons})} = \frac{P/h\nu}{P_{int}/h\nu} \quad (1-2)$$

Where P is the optical power emitted into free space. The light extraction efficiency is also known as the outcoupling efficiency (η_{oc}).

External Quantum Efficiency (η_{ext}). EQE is one of the most important factors in evaluating the performance of both OLEDs and QLEDs. It is the ratio of the number of photons emitted by the LED in the viewing direction to the number of electrons injected into the device⁴⁴, as showing below:

$$\eta_{ext} = \frac{(\# \text{ of emitted photons per second})}{(\# \text{ of injected electrons per second})}$$

$$= \frac{P/h\nu}{I/e} = \eta_{int} \times \eta_{extraction} \quad (1-3)$$

Power Efficiency (η_{power}). The power efficiency can be expressed as:

$$\eta_{power} = \frac{\# \text{ of photons emitted externally} \times h\nu}{IV} = \frac{P}{IV} \quad (1-4)$$

Where V&I are the external voltage and related current, respectively.

Color Rendering Index (CRI), Luminous Efficacy of optical Radiation (LER) and Luminous Efficiency (LE). CRI represents the ability of an emitter to reveal the colors of the body being irradiated by giving values varying from -100 to 100. The widely used incandescent bulb has a perfect color rendering capability. For indoor lighting, a high CRI at least higher than 80 is needed¹⁰. LER gives the quantitative evaluation of the device performance by presenting the ratio between the relative optical power of spectra perceived by human and the total power, while LE represents the same optical power to the electrical power. Therefore the units of LER and LE are lumen/(optical Watt) and lumen/(electrical Watt), respectively⁶⁶. They can be calculated by:

$$LER = \left(683 \frac{lm}{W_{opt}} \right) \frac{\int P_{opt}(\lambda) v(\lambda) d\lambda}{\int P_{opt}(\lambda) d\lambda} \quad (1-5)$$

$$LE = \left(683 \frac{lm}{W_{opt}} \right) \frac{\int P_{opt}(\lambda) v(\lambda) d\lambda}{VI} \quad (1-6)$$

Where $P_{opt}(\lambda)$ is the spectral density and $v(\lambda)$ is the eye sensitivity function, I and V are the current and applied voltage through the device, respectively.

1.3.2 Experimental setups

Since efficiencies are the primary performance metrics in the investigation of QLEDs, correct measurements are of great importance⁶⁷. If we assume that the emission spectra from LEDs with thin film structure follows the Lambert's law, then the key factors, including EL intensity versus applied voltage, EQE, power

efficiency (PE) and current efficiency (CE) can then be measured and calculated. In our lab, we use a PhotoResearch Spectroscan™ PR705 spectroradiometer and a programmable Yokogawa GS610 source measurement unit combined with an un-mounted photodiode in close contact with the active area of QLED to evaluate its performance⁶⁸. To be specific, the photodiode used here is to obtain the photo current regarded as the EL emission from QLED while the electrical current through the device is acquired simultaneously. Next, the absolute EL spectrum obtained from PR705 together with the two currents mentioned above will give the EL intensity, EQE, PE and CE by further calculations based on our customized LabVIEW package.⁶⁹⁻⁷¹

Figure 1-5. (a) YOKOGAWA GS610 measurement unit and (b) PhotoResearch Spectroscan™ PR705 spectroradiometer.^{72, 73}

1.4 Advantages of quantum dot-based LEDs

Here one might still ask such questions like why we prefer using quantum dots as the active material in light-emitting diodes, or what are their superiorities over other LEDs? The following descriptions might give reasonable answers in detail.

a) Pure, Saturated and tunable colors

One of the most interesting properties of QDs is their tunable wavelength, which should be attributed to the quantum-size effect⁷⁴. When the dimension of the bulk semiconductor decreases to nanometer-size range, especially around the Bohr

exciton radius, the energy levels will quantize, leading to significant changes of their physical properties, as shown in Figure 1-6⁷⁵. The confinement of electron-hole pairs also results a blue-shift in the emission spectra when decreasing the size⁷⁶. High purity atomic emission-like spectra are also achieved because of such confinement, therefore rendering a narrow linewidth compared with organic dyes⁷⁷. Figure 1-7 (a) shows the tunable and pure color emission from QDs with different size and compositions. The full-width half-maximum (FWHM) of CdSe-based core-shell QDs is as narrow as 30 nm or less, identifying them as superior luminescent emitters with saturated color.

Figure 1-6. Evolution of the electronic structure of inorganic semiconductors from bulk material to QDs of different size.⁶⁷

Figure 1-7 (b) demonstrates the potential coordinate of QD colors in the Commission Internationale de l'Eclairage (CIE) chromaticity diagram⁷⁸. It shows that the highly pure and saturated colors of QDs make it possible to properly choose red, green and blue-color QLEDs to form a bigger triangle than the high-definition television (HDTV) standard. Another advantage that QDs possess

while organic emitters do not have is that the spectrum of QD can extend to the NIR (near infrared) region, which is of current interest for active illumination for gesture recognition applications because the NIR is invisible to human eyes, therefore reducing the disturbance⁶⁷.

Figure 1-7. (a) Photoluminescence spectra of QDs showing narrowband emission across the visible regions; (b) CIE diagram showing the spectral purity of QDs.^{44, 78}

b) Cost-efficient manufacture

The synthesis of QDs often introduces some organic ligands onto their surface (-TOP, -oleic acid, etc.^{79, 80}), which is beneficial for their solubility into variety of organic solvents. These surface ligands enable the use of cost-efficient techniques for QDs deposition. Spin-coating, inkjet printing, micro-contact printing are commonly used for the QLED fabrication^{23, 28, 38, 39, 81-84}. Figure 1-8 shows two examples for QD deposition techniques and the corresponding QLEDs are also illustrated^{30, 81}.

Figure 1-8. (a) Schematic diagram of contact printing process; (b) Schematic illustration of transfer printing; (c) & (d) are the corresponding flexible and RGB QLEDs, respectively.^{30, 81}

The solubility of QDs in various solvents enables the all-solution process for QLED fabrication, therefore decreasing the manufacturing cost significantly^{36, 38}. For example, Yang et al. reported green and blue-emitting QLEDs with high EQEs both by all-solution process^{26, 85}. The green-emitting device consists of solution-processed films as charge transport layers and QD as emitting layer, highlighting with a maximum current efficiency of 40 cd/A with peak EQE of 12.6%, as shown in Figure 1-9.

Figure 1-9. Schematic diagram of solution-processed QLEDs, HRTEM picture of QDs, photograph of QLED under 8 V and the EL spectrum of the device, respectively.²⁶

c) Stability

Semiconductor QDs, as the inorganic nanocrystals, possess superior photostability than organic luminophores. However, bare QDs will degrade significantly resulting from photo-oxidation and photo-bleaching effects⁸⁶. What's more, the surroundings around QDs play important roles in modifying the optical and electrical performance of QDs, such as oxygen, humidity, the adjacent layers, the wavelength and intensity of the illuminated light⁸⁷⁻⁹³. Therefore, researchers introduce chemical composition graded shells to passivate surface defects and traps and confine electron-hole pairs inside cores⁷⁹. These QDs with shells exhibit high quantum yield because of the suppression and confinement, which is beneficial for QLEDs. Recently, “Giant” QDs are also synthesized for applications in QLEDs. Bhola N. Pal et al. have found that the device performance significantly increased simply by adding more shell layers (from 4 to maximum 16 layers of CdS). The device with the thickest shell exhibits an EQE and luminance of 0.17% and 2000 cd/m², respectively⁹⁴. The suppression

of energy transfer and Auger recombination are the main contributions of the thick shells, therefore increasing the device performance^{95, 96}. Coincidentally, Lee et al. synthesized so far the biggest Cadmium-based green-emitting QDs with a diameter of 12.7 nm. It has been demonstrated that an additional ZnS shell can act as an effective passivation layer as well as an energy barrier. The resulted QLED shows the highest EQE of 12.6% in green QLEDs with a peak current efficiency over 40 cd/A²⁶. In 2015, X. G. Peng et al. reported their red QLED on *Nature*, with the best T₅₀ lifetime of 100,000 hours, making the lifetime of their QLED comparable to the best OLED with vacuum deposition⁴¹.

Meanwhile, using inorganic semiconductor films/nanoparticles as charge transport layers to replace organic counterparts is a crucial step to increase the device stability. In our group, X. Y. Yang et al. applied WO₃ and ZnO nanoparticles to fabricate all-solution QLED with hybrid structure. By precisely modifying the device architecture, the operational lifetime can reach to 95 hours. This device shows an improved lifetime compared with that of the organic counterpart, as shown in Figure 1-10 (a)&(b).

Figure 1-10. (a) Schematic diagram of inorganic QLED; (b) Lifetime characteristics of inorganic nanoparticle QLED and standard one.³⁸

Based on the aforementioned advantages of QDs and QLEDs such as spectrally

narrow emission and size tunability, wide color gamut coverage, solution-process compatibility and better stability, researchers are devoting themselves to improve the performance of QLEDs. With the QLED becoming a competent candidate as backlights and emitters for flat-panel displays (FPD), and with the global flat-panel displays market is expected to reach \$110 billion by 2017⁹⁷, there is no doubt that QLEDs will receive more attentions in the area of solid-state lighting and displays. What's more, in the future, the goal is to bring QD electroluminescent devices into the realm of projection and lasing⁶⁷.

Chapter 2 Literature Review and Objectives

2.1 Revolution of quantum dot-based LEDs

2.1.1 Origin and early development

The first demonstration of the electroluminescence from QDs in a device was reported by Colvin et al. from Lawrence Berkeley Laboratory and UC Berkeley in 1994⁴⁰. They reported a hybrid organic/inorganic electroluminescent device. It emits light from both organic p-paraphenylene vinylene (PPV) and cadmium selenide (CdSe) QDs by the recombination of holes injected from PPV and electrons from nanocrystals, respectively. The EL spectrum shows the domination of CdSe emission at low voltages and the enhancement of green emission from PPV with the increasing applied voltages. Meanwhile, due to the quantum confinement effect, the emission wavelength could be effectively tuned by adjusting the diameter of nanocrystals⁹⁸⁻¹⁰⁰. The device (ITO/PPV/CdSe QDs/Mg) shows a maximum luminance around 100 cd/m². Although the external quantum efficiency is as low as 0.001% -0.01% because of the inefficient charge injection and mismatched energy diagram; this report definitely pointed the way to develop QD-based electroluminescence devices. Next, B. O. Dabbousi and M. G. Bawendi et al. reported a similar work, discussing the temperature-dependent electroluminescence from CdSe QDs mixed with poly(9-vinylcarbazole) (PVK) and an oxadiazole derivative (t-Bu-PBD), sandwiched between ITO and Al electrodes¹⁰¹. Two years later, the same group from UC Berkeley demonstrated an improved device performance by applying CdSe/CdS core/shell structure QDs as the light emitting material. The EQE reaches 0.22% with a peak luminance over 600 cd/m². What's more, this device has a low turn-on voltage of 4V and a lifetime of hundreds of hours¹⁰². Meanwhile, other reports also demonstrated the similar structures with moderate EQE and similar operation lifetime¹⁰³. It can be noticed that the reasons for the low efficiencies of these early QLEDs should be

ascribed in two aspects: (1) the low internal quantum efficiency of the emitters and (2) the charge injection imbalance because of the lack of electron injection/transport layer and the improper choice of hole transport layers.

Figure 2-1. (a) CdSe@CdS core/shell nanocrystal energy diagram. (b) Device configuration (inset) and absorbance and EL from materials.¹⁰²

2.1.2 The rapid expansion

A breakthrough was achieved by S. Coe et al. from Massachusetts Institute of Technology in 2002. By utilizing the monolayer CdSe@ZnS QDs with high efficiency and selecting suitable charge transport layers, their device with a structure of glass/ITO/TPD/QDs/Alq₃/Mg:Ag demonstrated a CE of 1.6 cd/A with a peak luminance of 2000 cd/m², a 25-fold improvement over the previously best data^{102, 104}. In this device structure, TPD and QDs were sequentially spin-casted onto the ITO substrate and the Alq₃ acting as electron transport layer was thermally evaporated on top of the monolayer of QDs. By modifying the thickness of each layer of the device, balanced charge injection was fulfilled, giving an unprecedented high EQE of 0.52%. Later, the same group reported a higher EQE up to 2% by developing a new method for forming large-area ordered

monolayers of colloidal QDs by spin-casting and the following phase separation^{83, 104}. It has to be noticed that all these QLEDs utilized organic materials as both charge transport layers, resulting in poor color purity and stability of operating device, and making them not comparable with OLEDs at that time. Therefore, researchers attempted to find alternatives as replacement of organic materials for charge injection and transport. In 2006, J. M. Caruge reported organic/inorganic hybrid QLEDs by using sputtered NiO as a hole transporting layer⁶⁵. The emitting layer was sandwiched by NiO and Alq₃, giving a peak external quantum efficiency of 0.18% by optimizing the resistance of NiO film to improve the charge balance inside the device, as shown in Figure 2-2 (a)&(b). Furthermore, electron transport layer based on metal oxide was also demonstrated by the same group. By radiofrequency-sputtering NiO as HTL and ZnO:SnO₂ as ETL (as presented in Figure 2-2 (c)&(d)), the all-inorganic QLED exhibits a peak brightness of 1,950 cd/m². This work with maximum EQE reaching 0.1% demonstrated that the inorganic metal oxides can act as the CTLs in QLEDs to maintain the performance as well as enhancing the robustness and environmental stability of QLEDs¹⁰⁵. As a result, more and more researchers are focusing on using metal oxides as the CTLs for the QLED fabrication.^{27, 64}

Figure 2-2. (a) The schematic representation and (b) band diagram of NiO-based QLED; (c) Schematic diagram of the structure and (d) corresponding energy band diagram of the all-inorganic QLEDs.^{65, 105}

With the improvement of QD synthesis and the innovation of charge transporting materials, white-emitting QLEDs were demonstrated simply by mixing red, green and blue QDs inside the hybrid organic/inorganic structures²⁴. P. Anikeeva reported white QLEDs based on the mixture of QDs with different emission wavelengths²⁴. For each monochrome QLED, the maximum EQEs are 1.6% for red, 0.65% for green and 0.35% for blue devices, resulting a high EQE of 0.36% for white QLED and a maximum brightness of 830 cd/m² with a CRI of 86. After that, Q. Sun et al. reported multiple-color QLEDs with the corresponding highest luminance at that time²⁷. They introduced PEDOT:PSS and poly-TPD as the HTL and Alq₃ as the ETL for efficient charge injection. Meanwhile, solution-processed blue QLED was reported by Tan et al., showing a low operating voltage of 5.5 V with a high brightness of 1600 cd/m².¹⁰⁶ At the same time, P. Anikeeva et al. investigated the mechanism of the organic/inorganic QLEDs. They observed a 50% enhancement of the EQE for the device which imbedded QD monolayers

into the hole transporting layer. By precisely controlling the region of exciton formation and the utilization of the energy transfer, the luminescent efficiency reached 2.3% with TPD and Alq₃ as charge transporting layers¹⁰⁷. Furthermore, the same group fabricated a series of QLEDs with tunable emitting wavelength over the entire visible spectrum from 460 nm to 650 nm by choosing the wide band-gap organic charge transporting layers, giving peak EQEs in the range from 0.2% to 2.7% corresponding to different colors²⁸. They also mentioned that high-EQE blue QLED remains a challenge. However, the demonstrations of the wide spectrum coverage justify the potential of using QLEDs in lighting and display applications.

Figure 2-3. (a) Schematic diagram and (b) EL spectra of QLEDs (inset: images of red, green and blue device).³⁶

In 2011, Qian et al. reported efficient QLEDs by using solution-processed multilayer structures consisted of organic HTL and zinc oxide (ZnO) nanoparticles (NPs) as the ETL³⁶. ZnO NPs have been proved to improve the electron injection and decrease the turn-on voltage⁶⁴. Their devices demonstrated maximum luminance of 4,200 cd/m², 68,000 cd/m² and 31,000 cd/m² with power efficiency of 0.17 lm/W, 8.2 lm/W and 3.8 lm/W for blue, green and orange-red QLEDs, respectively (shown in Figure 2-3 (a)&(b)). These values were among the highest during that time. One year later, Kwak et al. demonstrated further

improved device performance by applying inverted structure with ITO/ZnO NPs/QDs/4,4'-Bis(N-carbazolyl)-1,1'-biphenyl(CBP)/MoO₃/Al. The maximum brightness reached 23,040, 218,800 and 2,250 cd/m² with EQEs reaching 7.3%, 5.8% and 1.7% for red, green and blue QLEDs, respectively.³¹ Further, in 2013 and 2014, respectively, Yang's group demonstrated the highest EQEs of 7.1% and 12.6% for blue and green QLEDs with the modified recipes of QD synthesis^{26, 85}. In both devices, they highlighted the role of "thick-shell" in improving the performances including current density, brightness, luminance efficiency and power efficiency by suppressing the non-radiative energy transfer and confining both electrons and holes in the core to enhance the wavefunction overlap.

For red QLEDs, in 2013, a high EQE up to 18% was reported by B. S. Mashford et al. from QD Visions, Inc., using an inverted hybrid organic/inorganic structure²⁵. This report manifests that for the first time the efficiencies and brightness of QLEDs can be comparable with the state-of-the-art OLED performance. Further, in 2014, X. G. Peng et al. published their work demonstrating the highest EQE up to 20.5% with an incredibly low turn-on voltage at 1.7 V, low efficiency roll-off and long operation time more than 100,000 hours at an initial brightness of 100 cd/m² under encapsulation⁴¹. Later on, Y. Yang et al. reported red, green and blue QLEDs with EQEs all over 10%, which is a remarkable milestone in this field.⁴² They invented a new method to precisely tailor the structure of QDs in order to improve the charge injection and transport in QLEDs. Therefore, the performance are comparable, or even higher with the state-of-the-art OLEDs¹⁰⁸⁻¹¹⁰. Figure 2-4 (a) to (d) shows red, green, blue and white QLEDs with the highest EQEs to date, respectively.^{26, 33, 41,}

Figure 2-4. The reported red (a), green (b), blue (c) and white (d) QLEDs with highest efficiencies up to date.^{26, 33, 41, 85}

The aforementioned literatures demonstrate that, in only twenty years, the external quantum efficiency of QLEDs has increased from less than 0.01% to over 20%, a 2,000-fold improvement with higher luminance, current and power efficiencies and more stable operation lifetime, which make QLEDs a comparable competitor to OLEDs. These improvements further supported that QLEDs can act as the alternative to compete with more advanced electroluminescent technology for applications in solid-state lighting and displays.^{44, 58, 59, 67}

2.2 Synthesis of quantum dots (QDs) and fabrication techniques of quantum dot-based LEDs

2.2.1 Synthesis of quantum dots

Quantum dots, which are used as emitter in QLEDs, mainly include small inorganic semiconductor cores with a diameter less than 10nm and covered by different wide band-gap inorganic semiconductor materials as shells with organic ligands coated outmost, as shown in Figure 2-5(a). The universal and standard method of synthesizing QDs is based on the pyrolysis of organometallic precursors, where such solvents are injected into the hot organic coordinating solvent under varied temperatures (120-360 °C)^{79, 80, 111}. Then, by decreasing the reaction temperature swiftly, the nucleation of the core and growth of the outer shell induced by the precursor injection shall be forcibly prohibited. By comprehensively tuning the reaction conditions- including the temperature, reaction time and the concentrations/compositions of precursors, the size of QDs can be precisely tuned (for CdSe QDs in a range of 1.5–12 nm¹¹¹). The size of the small QDs is equal or similar to the Bohr exciton radius of the bulk semiconductor; therefore resulting in the quantized energy levels instead of the continuous ones (as shown in Figure 1-6), showing narrow spectra. What's more, because of the organic ligands, the synthesized QDs are highly mono-dispersed and soluble in lots of non-polar solvents (such as toluene, chloroform, hexane, etc.), exhibiting superior quantum efficiency^{25, 26, 36, 41, 85}. Currently, cadmium-based QDs dominate the fabrication of visible QLEDs while near-infrared QLEDs comprising lead chalcogenide QDs¹¹², as shown in Figure 2-5(b). Meanwhile, it should be highlighted that silicon (Si)-, indium phosphide (InP)- and CuInS₂/ZnS-QLEDs are also reported recently^{37, 60, 113-117}. Although these devices give inferior performance compared with Cd-based QLEDs, such cadmium-free QLEDs could act as alternative choices for applications in solid-state lighting and displays in terms of getting rid of the toxicity of cadmium.

Figure 2-5. (a) Structure (left) and band diagram (right) of gradient CdSe@ZnS QDs. (b) PL spectra of core-shell colloidal QDs with different compositions with a TEM image of a typical CdSe QDs (lower inset).^{44, 80, 118}

2.2.2 The fabrication of quantum dot-based LEDs

With the evolution of QD synthesis, numerous fabrication techniques aiming to transfer QD solutions into stacked layers inside QLEDs has concomitantly developed and updated in the past two decades. Nowadays, including the spin-coating technique, phase separation, contact printing, inkjet printing and electrophoretic deposition are widely used^{23, 28, 30, 81-84, 119-127}, which shall be discussed in details as shown below.

(a) Spin coating

Uniform and homogeneous films with different thicknesses can be deposited by spin coating, especially on flat substrates. By modifying the concentration of solution, the rotating speed and time, the film thickness can be precisely controlled. The film thickness is reversely proportional the spinning angular speed. One thing to be noted is that the orthogonal solvents must be used to avoid the destruction of underlying layers when spin coating the overlaying layers; otherwise the solution of the upper layer might dissolve the lower films. For example, in a typical solution-processed QLED procedure, PVK dissolved in

chlorobenzene is spin coated onto PEDOT:PSS layer first, then the QDs dispersed in toluene are spin coated subsequently. Spin-coating is not only the most cost-effective deposition technique but also the most common procedure for fabricating QLEDs with high efficiency; in fact, the reported highest QLEDs are all fabricated by spin coating, at least for some layers^{26, 41, 85}.

(b) Contact printing

Although it has been widely used for fabricating QLEDs, spin coating has certain limitations: it makes patterned QD layers impossible and it requires the orthogonal solvents to dissolve different materials for film deposition, which limits the choice of solvents and materials as well⁸¹. Contact printing, on the other hand, solves these problems to some extent. In contact printing technique, poly(dimethylsiloxane) (PDMS) is often used as a stamp for transferring QDs because of its ability to make conformal contact with surfaces over large areas⁸². According to Kim *et al.*⁸¹, the QD printing process follows 4 steps: (1) patterned PDMS is acquired by a mold; (2) a thin film is used to coat the PDMS; (3) the modified stamp is further decorated by QD layers; (4) dried QD layers are transferred to substrate. Figure 2-6(a) shows the four-step contact printing process⁸¹. On the basis of this, Kim *et al.* demonstrated a full-color QD display with a size of 4 inch by using a similar transfer contact-printing technique, proving a further step for the commercialization of QD displays (Figure 2-6(b))³⁰.

Figure 2-6. (a) Contact printing process with different procedures; (b) Electroluminescence image of 4-inch full-color QD display.^{30, 81}

(c) Inkjet printing

Liquid materials can be deposited by inkjet printing without the need of mask. Compared with the techniques mentioned above, inkjet printing is a more attractive method, especially for large-area QD layer deposition because of the limited material usage and multi-layer formation with controllable resolution¹²⁴. What's more, inkjet printing can deposit QD patterns with high accuracy easily up to tens of micrometer range. Haverinen et al. reported series of works using inkjet printing technique to fabricate patterned QLEDs^{84, 125}. Wood et al. also demonstrated print deposition of patterned multicolor QD films and their applications in the fabrication of robust, bright and full-color displays driven by alternative current, as shown in Figure 2-7, proving this technique to be suitable for fabrication of patterned QLEDs¹²⁴.

Figure 2-7. RGB QLED based on inkjet printing technique.¹²⁴

(d) Phase separation

In spin coating process, orthogonal solvents must be used to deposit the adjacent layers in order to avoid inter-mixing. Therefore the limited choices of solvents confine the application of spin-coating technique. Phase separation, however, can be regarded as a combination of two-step spin coating processes to form two adjacent layers simultaneously. It is a very simple process relying upon the solvation of both organically capped semiconductor QDs and the organic material to be used as CTL⁸³. As depicted in Figure 2-8, first, a mixed solution containing QDs and organic materials is formed and further spin coated onto the substrate; then the QDs will move to the upper part of the mixed solutions spontaneously during the annealing process. The quality of the bilayer film depend on several factors including QD size and shape, the mixed solution concentration and solvent ratio, etc. Phase separation has been shown to be a useful technique for fabricating highly efficient QLEDs and other optoelectronic devices^{63, 128}.

Figure 2-8. Schematic procedures of QLED based on phase separation technique.⁸³

(e) Electrophoretic deposition (EPD)

In electrophoretic deposition method, two electrodes are applied with voltage to form electric field to drive QDs move towards and deposit onto the electrodes, as demonstrated in Figure 2-9¹²⁷. Compared with spin coating, which the majority of QD solution was spun out of the substrate, EPD has the following advantages: first, EPD process is efficient in saving the initial colloidal QD solutions; second, multiple devices can be fabricated concurrently in one batch; what's more, electrodes with random constructions could be deposited with QD solutions by using EPD techniques, therefore extending the applications of QLEDs for special

requirements. Compared with spin-coating, phase separation and inkjet printing techniques, which QD layers are formed in a rapid speed, the speed of EPD is much slower, therefore the resulted QD film onto the substrate can be composed in a more energetically favorable structure, resulting in the improvement of QLED performance^{120-122, 126}. Song et al. demonstrated red QLEDs with thin and uniform colloidal QD films using EPD, proving this technique an alternative method comparing with spin-coating in QLED fabrication¹²⁷.

Figure 2-9. (a) Schematic diagram of EPD with (b) AFM topography image of QD films by using EPD method and (c) film thickness of 15 nm by EPD.¹²⁷

2.3 Classification and working mechanism of quantum dot-based LEDs

2.3.1 Classifications

It has been widely accepted that QLEDs can be classified by the chemical properties of the corresponding charge transport layers. Therefore, according to the description from Y. Shirasaki *et al.*⁴⁴, there are four types of QLEDs as shown in Figure 2-10, which will be introduced in details as below.

Figure 2-10. The classification of QLEDs in four types.⁴⁴

Type I: QLEDs with polymer charge transport layers. These devices belong to the earliest QLED type with a borrowed structure from polymer LEDs^{40, 101-103}. The basic structure is simple: CdSe core was sandwiched between polymer(s) and further two electrodes. Because of the low quantum yield of the bare CdSe core and its natural insulativity, type I QLEDs exhibited a low EQE (less than 0.01%) and low current densities⁴⁰. Later, the introduction of core/shell QDs improved the EQE to 0.22% with a luminance of 600 cd/m² for type I QLEDs¹⁰². However, the electroluminescence spectrum of type I QLEDs included not only QD emission but also the characteristic emission from adjacent polymers due to the inefficient exciton formation in QDs (Figure 2-11). Therefore, researchers quickly turned to other QLEDs with more reasonable structure configurations.

Figure 2-11. The EL spectrum under different applied voltages of type-I QLED with its structure shown in the inset.⁴⁰

Type II: QLEDs with organic small molecule CTLs. This type was firstly demonstrated by Coe et al. from MIT in 2002. The device consisted a monolayer of QDs in a bilayer OLED, giving the highest EQE of 0.5% at that time¹⁰⁴. In their design, QD monolayer was applied in order to “decoupling the luminescence process from charge transport through the organic layers”^{21, 107, 129}, which should be responsible for the performance enhancement. They used a phase separation method as mentioned before: a mixture solution of QDs and organic polymers which acts as hole transport layer is spin-coated onto the substrate; Because of the phase separation, the QD monolayer will be formed on top of the organic films spontaneously. Other novel methods are also applied to form a closely-packed QD monolayer in type-II QLEDs. Later, the same group reported QLEDs with tunable electroluminescence varying from blue to deep

red²⁸. Such type-II QLEDs achieved a maximum external efficiency of 2.7% with the orange-emitting QDs. This work, together with a reported CRI of 86 white QLED clearly demonstrated the possibility of type-II QLEDs in EL displays and solid-state lighting sources^{22, 24}.

Figure 2-12. (a) The structure of the first type-II QLED and (b) Energy band diagram of another type-II QLED.^{28, 104}

Incorporating a monolayer of QDs with an OLED structure effectively improved the efficiencies of type-II QLEDs. However, the use of organic materials as CTLs degrades the QLEDs, especially upon exposure to air and humidity¹³⁰. Therefore, in order to commercialize QLEDs products, protective encapsulation is necessary just like OLED technology, which increases the fabrication costs and impedes the realization of flexible QLEDs. What's more, because of the insulativity of organic semiconductors, the achievable current densities of QLEDs are limited, restricting their efficiencies and maximum brightness.

Type III: Inorganic CTL-based QLEDs. Using inorganic CTLs to replace the organic counterparts in type-II QLEDs can improve the device stability as well as the current density. In 2005, Muller et al. reported an inorganic QLED with a monolayer sandwiched between epitaxial-grown GaN²¹. The EQEs were between 0.001 - 0.01% because of non-optimal procedures and low doping levels of the top n-layer. Furthermore, radiofrequency (RF) sputtering was applied to

deposit inorganic metal oxide CTLs. Compared with organic counterparts, metal oxides are more conductive and tunable by changing the parameters of film growth. Caruge et al. reported the use of sputtered inorganic semiconductors as CTLs in QLEDs. NiO and ZnO:SnO₂ alloy were deposited as ETL and HTL, respectively¹⁰⁵. A higher current densities was achieved (exceeding 3.5 A/cm²) because of the adoption of metal oxides but with a lower EQE (less than 0.1%). The low efficiency can be explained by the deterioration of QD layer during sputtering¹³¹.

Other type-III QLEDs were also emerged with different excitation mechanism in the past few years. The capacitive structures have a dielectric film with a QDs layer in the center sandwiched by two contacts, as shown in Figure 2-13¹³². In such configuration, the CTLs are abandoned and whether the energy band is aligned or not doesn't matter. Although they exhibited inferior efficiencies, such devices offer another way for studying QDs excitation as well as the research focusing on the effect of external applied electric field¹³³.

Figure 2-13. (a) Device schematic diagram and photographs of green, orange and red AC devices; (b) EL spectra of AC QLEDs with CdSe-ZnS QDs.¹⁰⁴

Type IV: QLEDs with hybrid organic/inorganic CTLs. Just like the designation, these QLEDs apply both organic and inorganic materials as CTLs. Metal oxides like ZnO are the electron transport material while the organic

semiconductors act as the hole transport material. Such hybrid structures do not receive too much attentions until researchers find that high EQEs and brightness can be achieved by using solution-processed ZnO. Using this hybrid structure, all red, green and blue QLEDs achieved highest EQEs in the past few years. For red QLED, Dai et al. demonstrated an EQE of 20.5% by using ZnO nanoparticles as ETL and PEDOT:PSS with poly-TPD and PVK as HTLs, respectively, which greatly surpassed previous efficiencies⁴¹. Y. Yang's group reported a series of red, green and blue QLEDs with high EQEs over 10% by the structure of PEDOT:PSS/TFB/QDs/ZnO/Al⁴². All these devices with high EQEs utilize ZnO nanoparticles as ETL because of the superior electron mobility, better energy band alignment and its stability as the protection layer. Recently, using similar type-IV hybrid organic/inorganic structures, Bae et al. reported a full-color QLED display of 1.2 cm × 1.2 cm display panel³³. Red, green and blue QLEDs with narrow spectral FWHM are used as backlight with high color reproduction and solid-state lighting with a CRI over 92, as shown in Figure 2-4(d).

2.3.2 Working mechanisms

Depending on the thickness and position of the QD layer and compositions of other organic/inorganic layers, the mechanism of QD EL generation can be explained by either direct charge injection or energy transfer, or a combination of both.

In case of charge injection, just as its name implies, the charge transport layers (CTL) inject/transport electrons and holes into QDs respectively; an exciton is formed and subsequently recombined by emitting a photon. For energy transfer-based mechanism, on the other hand, the QLEDs must occupy other luminescent materials such as organic dyes and they should be very close to the QD layers^{129, 134-136}. The mechanism of energy transfer can be described as follows: First, the fluorophore forms an exciton under charge injection; then the energy is non-radioactively transferred to QDs by dipole-dipole coupling. It is hard to clearly

distinguish which mechanism should account for certain structures; actually in most cases both charge injection and energy transfer contribute to the electroluminescence of QLEDs¹³⁷. Figure 2-14 (a) to (d) gives four routes for exciton generation in QDs. And two possible QD excitation mechanisms happened in QLEDs are outlined in Figure 2-14 (e): charge injection and energy transfer⁴⁴. We can imagine that QLEDs with better efficiency and stability can be achieved by a better understanding of the mechanisms behind the electroluminescence QDs.

Figure 2-14. (a)-(d) Four ways for generating excitons in QDs. (e) Illustration of two mechanisms for QLEDs: green route for direct charge injection and recombination while blue curve for dipole-dipole non-radiative transfer.

2.4 Objective

Although the present QLEDs have obtained remarkable performance in terms of external quantum efficiency, current efficiency, power efficiency, color purity, wider color gamut coverage, etc., there still exist some drawbacks which might hinder the full commercialization^{26, 33, 41, 42, 44, 58, 67, 85, 138}. For example, those QLEDs which demonstrated the best device performance utilize Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) on top of ITO electrode for efficient hole injection without an exception⁴¹⁻⁴³. However, as an organic material, PEDOT:PSS often trends to acidly corrode the ITO electrode,

resulting in device instability and degradation¹³⁹. Therefore, it is of great importance to find alternative material aiming to further improve the long-term device durability.

Furthermore, reducing the material costs in fabricating QLEDs has practical and significant influence for the commercialization of QLEDs and earning more market share. As mentioned above, the disadvantages of PEDOT:PSS has engaged researchers in considering inorganic materials for hole-injection replacement^{38, 39, 65}. Metal oxides, such as nickel oxide (NiO), vanadium oxide (V₂O₅), tungsten oxide (WO₃) and molybdenum oxide (MoO₃) are introduced^{38, 39, 69, 140, 141}. Although similar performance has been demonstrated, the metal oxide film normally needs high-temperature annealing to acquire suitable transparency and conductivity¹⁴²; some of the metal oxide films require extra O₂-plasma treatment to optimize hole injection by the removal of the polymeric dispersing agent; such requirements are contradictory to the initial purpose of applying inorganic materials as a replacement for PEDOT:PSS.

On the other hand, in order to optimize the performance of QLEDs, charge balance is an important factor and much efforts have been made to improve it^{25, 41-43}. For example, B. S. Mashford et al. used inverted hybrid structure with ZnO film as electron transport layer and colloidal CdSe@CdS QDs as emitters to obtain the optimal charge transport balance²⁵. X. G. Peng incorporated a thin layer of PMMA with suitable thickness acting as buffering layer to block electron injection, achieving balanced charge injections and superior performance⁴¹. In normal QLED structure, by thermally evaporating the lithium fluoride (LiF) as the cathode interfacial layer with a thin thickness, the workfunction of aluminum as cathode can be elevated; therefore the electron injection shall be further improved^{80, 82, 94, 116}. However, due to its wide bandgap and insulation property, LiF requires rather high current for its successful deposition; and the thin thickness also brings in the uncontrollability during the fabrication. Hence, other

materials are highly expected to replace LiF for better device performance.

Therefore, to these ends, there still exist plenty of rooms and more efforts can be put in this realm regarding exploring alternative materials, developing advanced device structure, optimizing the charge balance of QLEDs and the realization of all-inorganic QLED. By improving device performance and stability, we can expect its commercialization in the future.

2.5 Major contributions

In general, there are four major contributions included in this thesis: the first part includes the use of a new cathode interfacial material named Phen-NaDPO for the substitution of LiF. High-performance QLEDs are demonstrated, proving the capability of this material in optoelectronic devices. The second part is the preparation of metal oxide film for its application in QLEDs as HIL in replacement of commonly-used PEDOT:PSS, showing comparable device performance with improved operation lifetime; In the third part, a commercial inorganic material is introduced as charge injection material in QLED; the device performance justifies the feasibility of this inorganic HIL and further raises promise for the possible commercialization. The fourth part demonstrates the successful fabrication of all-inorganic QLEDs with the best performance so far by using LiF as the buffering layer for charge injection balance and interfacial optimizations. The detailed contributions are summarized below.

- By utilizing the superior property such as the high electron transport mobility and high glass transition temperature (T_g), a novel material Phen-NaDPO which has been successfully demonstrated in OPV is applied in QLED as the cathode interfacial material. With the introduction of this CIM, the resulted device achieves an improved device performance compared with the control device in terms of the maximum brightness, turn-on voltage, EQE and CE. Further, the comparison on the performance of this device with the

commonly used LiF-based device shows the similar electrical characteristics with a higher efficiency of the CIM-based QLED. The UPS measurements demonstrate that the deposition of Phen-NaDPO can help to lift the workfunction of cathode, therefore reducing the electron energy barrier and resulting in the improved performance. Furthermore, higher EQE reaching 8.5% under a peak CE over 29 cd/A has been achieved by the bilayer of LiF and Phen-NaDPO as the CIMs together. The analysis based on the comparisons of the electrical characteristics of the single-carrier devices as well as the UPS measurements of the different material system demonstrate the optimized charge balance, resulting in the enhanced performance.

- QLEDs with high performance have been fabricated based on copper oxide (CuO) as the hole injection material with a facile solution process. By optimizing the conditions of CuO film deposition, an extraordinary ability for hole injection was achieved. The resultant device shows an EQE reaching 5.4% and a peak luminance over 70,000 cd/m². These performance are much higher than those of the device without CuO as the HIL. Furthermore, compared with the control device based on the PEDOT:PSS HIL, the key parameters including EQE, CE and PE are better or at least commensurate. The lifetime measurement further demonstrates a better device stability for CuO-based QLED.
- An inorganic semiconductor copper (I) thiocyanate (CuSCN) is introduced as a solution-processable HIL in QLEDs. Due to the deep valance band maximum with a value of 5.5 eV, CuSCN acted as the hole injection material in QLED decreased the turn-on voltage to 3.4 volt, which is 0.8 V lower compared with the device based on the commonly used PEDOT:PSS (4.2 V). The optical measurement demonstrates the moderate transparency of CuSCN film. What's more, CuSCN-based QLED presents slightly better performance compared with PEDOT:PSS-based QLED. Considering the fact

that this material is cheap and abundant, in this work, the successful demonstration of this CuSCN as HIL with straightforward preparation method can provide guidelines and prospects for the development of reliable all-inorganic QLEDs and possible commercial applications.

- All-inorganic QLEDs with optimized device configuration are fabricated and characterized, demonstrating a peak brightness and an EQE with values of 7,600 cd/m² and 1.74%, respectively, 4-fold higher than the previous luminance record and 9-fold higher than the previous EQE value^{105, 131}. Such unprecedented performance should be attributed to the optimized charge balance and the inhibition of the quenching effects of inorganic CTLs on QD emission by using solution-processed CTLs and the insertion of LiF as the buffering layer between the active layer and the adjacent ZnO film as the electron transporting layer. This study offers constructive insight into the performance enhancement of inorganic electroluminescent devices.

2.6 Organization

This thesis is divided into 7 chapters with brief descriptions given as below.

Chapter 1 gives a brief introduction of QLEDs. First, the background of developing QLEDs for solid-state lighting and display is described from a board perspective, following by the introduction of basic device configuration of QLEDs. Furthermore, useful concepts, metrics and the experimental setups are explained and introduced in this chapter, with the lists of the advantages of QLEDs over other electroluminescence counterparts at the end of this chapter.

In chapter 2, a review of related literatures and the aim of this thesis are thoroughly depicted in four parts. The first part includes the origin and developments of lab-based QLEDs chronologically as well as the illustration of the best device performance so far. The second part introduces the QD synthesis technique and the thin-film fabrication methods of QLEDs. The classification

and working mechanism of QLEDs are shown in the third part of this chapter. The last part of this chapter states the objective and major contributions of this thesis.

Chapter 3 introduces the demonstration of an alternative cathode interfacial material as a replacement of LiF in QLEDs. We utilize a new organic material named Phen-NaDPO in QLED for the first time. Owing to its high carrier mobility and glass transition temperature, the better device performance of Phen-NaDPO-based QLED in terms of the luminance and efficiencies (EQE, CE and PE) are attained compared with those of the pristine Al-based device. Furthermore, the Phen-NaDPO-based device presents higher EQE and CE compared with those of the LiF-based device. Moreover, by combining the two CIMs together, better result is achieved with a higher device external efficiency of 8.5% in the bilayer CIM-based device. A detailed explanation is given at the end of this chapter.

Chapter 4 demonstrates and characterizes the application of solution-processed copper oxide (CuO) thin film as HIL in QLEDs. This metal oxide HIL can be easily synthesized and prepared under low temperature. With the optimization of film preparation and device fabrication, the best CuO-based QLEDs are illustrated, showing a high EQE of 5.4% with maximum brightness over 70,000 cd/m^2 . Compared with the control PEDOT:PSS-based device, higher EQE, comparable luminance and current efficacy are obtained. What's more, in this chapter, the CuO-based QLED shows improved device stability than PEDOT:PSS-based device according to the device lifetime measurement. These results validate CuO as an alternative solution-processed hole injection materials to replace PEDOT:PSS.

Next, in chapter 5, we introduce the utilization of a commercially-available inorganic semiconductor copper thiocyanate (CuSCN) as the HIL in QLEDs. The advantages of this material such as low cost, high work function, good

transparency, superior stability and better hole mobility are demonstrated. The turn-on voltage of CuSCN-based QLED is significantly decreased to 3.4 V as compared with PEDOT:PSS-based ones. Besides, CuSCN-based QLED presents better or at least comparable performance compared with PEDOT:PSS-based one in terms of brightness, EQE, CE, etc. We also mention that the successful demonstration of this solution-processed HIL in QLEDs may provide guidelines and prospects for the development of reliable all-inorganic QLEDs and their possible commercialization.

Chapter 6 gives the demonstration of all-inorganic QLEDs with record high electroluminescence efficiency and peak luminance. Solution-processed metal-oxide films are introduced to realize the inorganic QLEDs while LiF is inserted between the active layer of QDs and the adjacent ETL aiming for achieving the improved performance. To be specific, the inorganic QLED shows the record brightness of 7,600 cd m⁻² and an EQE of 1.74%, respectively. These findings suggest that the interfacial engineering is quite critical for improving QLED performance and this approach should be of great importance in understanding and designing high-performance inorganic QLEDs in the future.

Finally, chapter 7 summarizes the conclusions of this thesis and introduces the research plans in the future.

Chapter 3 Performance Improvement of Quantum Dot-Based Light-Emitting Diodes by Introducing A Cathode Interfacial Layer

3.1 Introduction

Since its debut on Nature by V. L. Colvin and A. P. Alivisatos at 1994⁴⁰, quantum dot-based light-emitting diodes (QLEDs) have been regarded as one of the promising competitors for the next-generation solid-state lighting and display technologies, mainly due to the full-visible-spectrum coverages by simple size-tuning, narrow full-width at half-maximum (FWHM) with saturated color expression on CIE chromaticity diagram and the potential to be fully solution-processed^{26, 36-39, 41, 42, 44}. There are already publications recently demonstrating that comparable levels of efficiency with better color saturation and lower costs can be achieved by QLEDs over their long-term counterpart - organic LEDs (OLEDs)^{41, 42}. As can be observed from most of the reported QLEDs with high efficiency, solution process (spin-coating in most case) and thermal evaporation techniques are alternatively or together utilized for device fabrication; for spin-coating, in order to form layer-by-layer architecture, orthogonal solvents are compulsorily needed to avoid interlayer mixing and precious thickness control of different films can therefore be achieved; while thermal evaporation is deemed as a method under certain circumstance the underlying active layers have to be protected from possible degradation brought by the additional solution process, and smooth layers can be deposited morphologically^{25, 38, 39, 41}.

For QLED fabrication process with thermal evaporation, lithium fluoride (LiF) is frequently used as the cathode interfacial material (CIM) to improve the electron injection by reducing the work function of the cathode (aluminum in the most cases)^{80, 82, 94, 116}. Several theories have been proposed to explain such carrier injection improvement, including the reduced injection barrier resulted

from the band bending¹⁴³, the tunneling theory¹⁴⁴ and the decreased surface potential of cathode resulted from the large dipole moment of LiF¹⁴⁵. Although improved electron injection can be achieved by this material, the insulating property of the inorganic LiF could result in very high temperature (in our lab, a temperature over 600 °C is always required) during thermal evaporation process; what's more, such high evaporating temperature might deteriorate the underlying organic layers, resulting in the reduced device performance¹⁴⁶. Besides, because the thickness of LiF used in the device is very thin (less than 1 nm), there exists a process uncontrollability which would lead to an inferior reproducibility¹⁴⁷. These abovementioned disadvantages definitely cast doubts in continuing the use LiF as cathode interfacial material. Therefore, other materials for cathode modification purpose, including inorganic metal compounds such as cesium carbonate¹⁴⁸, cesium fluoride¹⁴⁹ and low work-function metals including magnesium^{65, 83, 107} and calcium^{27, 115} have been reported to reduce the injection barriers and improve the device performance. However, these materials can hardly achieve comparable device performance as LiF does^{27, 65}.

In this work, we introduce an efficient cathode interfacial material (CIM) with a name of 1,10-phenanthroline-(2-naphthyl)diphenyl-phosphine oxide (Phen-NaDPO), aiming to improve the device performance. Phen-NaDPO possesses an electron mobility of $3.9 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (at $E \sim 8 \times 10^5 \text{ V cm}^{-1}$) and a glass transition temperature (T_g) of 116 Celsius degree; More inspiringly, this material has been successfully demonstrated as a versatile CIM by improving the power conversion efficiency (PCE) in organic photovoltaics¹⁵⁰. Here, in our QLED devices, first of all, by depositing this material between the electron transporting layer and the cathode, better device performance including external quantum efficiency (EQE), current efficiency (CE) and power efficiency (PE) can be achieved when compared with these parameters of the device with pristine Al as the cathode; Secondly, the Phen-NaDPO device with further optimization shows

comparable maximum luminance with LiF-based device while the CE and PE are both improved compared with those of the latter. Furthermore, by incorporating Phen-NaDPO and LiF together as the buffering as well as interfacial materials, the device performs an even higher EQE of 8.5% with smaller efficiency roll-off under high current densities. In order to explain such improvements, ultraviolet photoelectron spectroscopy (UPS) measurement with the current density-voltage characteristics of the single-carrier devices are utilized and analyzed.

3.2 Experimental details

3.2.1 Preparation of quantum dots

A reported recipe with minor modifications were applied to synthesize the CdSe@ZnS core-shell quantum dots (QDs)²⁶. Briefly, the mixture of 0.14 mmol of cadmium acetate, 3.41 mmol of zinc oxide and 7 ml of oleic acid (OA) were loaded in a four-neck flask and heated to 100 °C under degassing with a pressure of 0.02 mTorr for 20 minutes. Then, 15 ml of 1-octadecene (1-ODE) was swiftly injected into the flask and the whole mixture was degassed and heated back to 100 °C to remove the air and moisture from 1-ODE. Then, inert gas was introduced to the system with a fast temperature increasing up to 310 °C. After the temperature was stable, 2 mmol of selenium (Se) and 2 mmol of sulfur (S) dissolved in 2 ml trioctylphosphine (TOP) was swiftly injected into the hot mixture, and the new system was left to react for 10 minutes to form the core-shell QDs. In order to coat an additional ZnS shell for high performance, 1.6 mmol of S dissolved in ODE (2.4 ml) was injected and the mixture was left to react for another 12 minutes. Then the injection of 9.5 ml Zn(OA)₂ was performed under the temperature of 270 °C. Next, 5 ml of TOP dissolving 9.65 mmol of S was slowly introduced into the mixture in a rate of 10 ml/min by a syringe pump. The outmost shell needed around twenty minutes to grow under this temperature. The raw QD solution in the flask was further purified and dispersed in toluene for later use in device.

3.2.2 Device fabrication and characterization

A standard cleaning procedure with ITO detergent, de-ionized water (DI-water), acetone and isopropyl alcohol (IPA) were used to sequentially clean the glass substrates with patterned ITO. For the device fabrication, poly (3,4-ethylenedioxythiophene)-poly-(styrenesulfonate) (PEDOT:PSS) was deposited first with a speed of 4000 rpm for 1 min and further annealed at 150 °C for half an hour as the hole injection layer, followed by 30 nm of poly(9-vinylcarbazole) (PVK) serving as the hole transport layer. The QD layer was deposited with a speed of 1000 rpm for 60s and subsequently annealed at 90 °C for 30 min on the ITO/PEDOT:PSS/PVK configuration. Then, the substrates were transferred into the evaporation chamber and on top of the QD layer, 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi), cathode interfacial material (LiF or Phen-NaDPO) and Al were sequentially thermal-evaporated under a base pressure of $\sim 2.0 \times 10^{-4}$ Pa. The effective area of the LED devices is 4 mm².

UPS measurement was performed by using X-Ray Photoelectron Spectroscopy (XPS) (VG Escalab 220i XL) with a He I (21.2 eV) gas discharge lamp. The current density-voltage (J-V) characteristics were measured using a programmable Yokakawa GS610 source measurement unit when an un-mounted silicon photodiode was in close contact to the active area of QLED to record the photocurrent. A PhotoResearch SpectraScan PR 705 spectrometer was applied to record the absolute electroluminescence spectra. The performance including J-L-V characteristics, EQE, CE, PE and CIE coordinate were then calculated and exported based on the measured data with our customized program. All measurements were performed at room temperature under ambient atmosphere without any encapsulation.

3.3 Results and discussion

3.3.1 Electrical properties of QLEDs based on CIM with different thicknesses

The normalized electroluminescence (EL) spectrum with emission peak wavelength centered at 522 nm with a full width at half maximum (FWHM) of 20 nm is shown in Figure 3-1(a). While Figure 3-2(b) demonstrates a device architecture of the QLED discussed in this chapter, where the CIM layer are inserted between the Al cathode and TPBi (the electron transport layer) to facilitate electron injection. For the first comparison, during the device fabrication, Phen-NaDPO was thermally evaporated before aluminum deposition while the control device with only aluminum as cathode is simultaneously fabricated. Figure 3-2(a) shows the current density-voltage-luminance (J - V - L) characteristics of QLEDs with both devices based on Al and Phen-NaDPO (with different thicknesses)/Al as cathodes, respectively. It can be straightforward noticed that the devices with Phen-NaDPO-decorated cathode show improved performance over the Al-only device (the black curves); to be specific, the best-performance of Phen-NaDPO-based QLED is achieved with the Phen-NaDPO thickness of 9 nanometers, giving a maximum luminance over 130,000 cd/m². The EQE and current efficiency (CE) as functions of the current density for these QLEDs are also given in Figure 3-2(b). The optimized Phen-NaDPO-based QLED demonstrates a peak EQE of 7.4 % and maximum CE of 24 cd/A while in contrast, the device with pristine Al as the cathode gives an inferior performance with a maximum EQE lower than 6% and lower peak brightness, as can be illustrated from Figure 3-2(a) and (b), respectively.

Figure 3-1. (a) Normalized electroluminescence (EL) spectrum (centered at 522 nm) and (b) the schematic illustration of QLEDs.

Figure 3-2. The performance comparison of Al-based and CIM/Al-based devices: (a) Current density-voltage-luminance (J-V-L) characteristics and (b) EQE and CE of these devices as functions of current density.

3.3.2 Device optimization and comparison

To moving forward, we compare the performance of the optimized Phen-NaDPO-based device with the LiF-based device to prove the feasibility of this material. As can be observed from Figure 3-3(a), a comparable J-V-L characteristic similar with those of the LiF-based device is achieved by the Phen-NaDPO-based QLED. As for the performance, the Phen-NaDPO-based QLED demonstrates both higher EQE (7.4 %) and CE (24.1 cd/A) than these parameters of LiF-based QLED with an EQE of 6.8% and a CE of 21.8 cd/A, as shown in Figure 3-3(b). It should be made clear here that even in optimized QLED with LiF as cathode interfacial material, charges cannot be well balanced because the electrons are more easily injected than the holes due to the high energy barriers encountered by holes from the anode side^{36, 65}. Therefore, we applied ultraviolet photoelectron spectroscopy (UPS) measurement to explain the role that Phen-NaDPO played in improving the performance of QLED. Figure 3-3(c) shows the

secondary-electron cut-off regions of the UPS spectrum of pure Al film and Phen-NaDPO on Al film, respectively. By using the equation (workfunction (WF) = $21.2 \text{ eV} - E_{\text{cutoff}}$)³⁹, we can get the WF of Al and Phen-NaDPO/Al, which are 3.5 eV and 3.3 eV, respectively. It means that the deposition of Phen-NaDPO onto the Al film can reduce the WF of the system effectively. To some extent, the reduced WF of cathode in QLED can decrease the barriers of electron injection, therefore the electron injection into active layers is facilitated and the device performance is improved^{143, 149}.

Figure 3-3. (a) Comparison of the current density-voltage-luminance (J-V-L) characteristics between LiF/Al-based and CIM(9 nm)/Al-based devices, respectively. (b) EQE and CE verse

current density characteristics of these two devices. (c) The secondary-electron cut-off region of UPS measurement of Al and Phen-NaDPO/Al films, respectively.

3.3.3 Discussion and results

Charge balance is always one of the most important factors when researchers want to fabricate QLEDs with high performance^{25, 38, 39, 41, 42, 151}. It has been well recognized that in QLEDs with regular structure (ITO as anode and metal as cathode), the injection of electrons and holes are not balanced due to the fact that electrons are injected spontaneously while holes suffer from energy barriers during its injection and transportation from anode mainly because of the deep valence-band energy level of our green quantum dots^{39, 41, 69, 152}. In order to balance the charges, one possible solution is to partially block the electron injection from cathode by inserting a blocking/buffering layer in the device configuration,¹⁵¹. Previous reports have applied poly (methyl methacrylate) (PMMA) and hole transport layers (TCTA, CBP, etc.) as electron blocking layers to achieve balanced charge⁴¹. In this work, the Phen-NaDPO was introduced as buffering layer between the electron transporting layer (TPBi) and cathode interfacial layer (LiF). Figure 3-4(a) shows the EQE-CE-current density relationships of LiF-based and Phen-NaDPO/LiF-based devices, respectively; higher EQE (8.5%) and CE (over 29 cd/A) are achieved with the device based on the combined cathode configuration (Phen-NaDPO/LiF/Al), demonstrating the positive effect of this material.

Figure 3-4. (a) EQE and CE versus current density of the devices with different cathode configurations. (b) Electrical measurements on the current density-voltage (J-V) curves for the single-carrier devices (electron-only and hole-only). (c) UPS spectra of the secondary electron cut-off regions of LiF/Al and Phen-NaDPO/LiF/Al films, respectively and (d) Schematic illustration of electron injection from LiF/Al (black) and Phen-NaDPO/LiF/Al (red) cathodes into TPBi and active layer.

In order to prove that a more balanced charge injection due to the decreased electron injection is achieved with the insertion of this buffering layer, we fabricated a set of electron-only devices with a structure of ITO/ Cs₂CO₃ (2 nm)/QDs/TPBi/(LiF or Phen-NaDPO/LiF)/Al and hole-only device (ITO/PEDOT:PSS (35 nm)/PVK (40 nm)/QDs (40 nm)/Au(300 nm)) device, respectively. Figure 3-4(b) shows the current density-voltage (J-V) curves of the single-carrier devices. It should be mentioned that the thicknesses of all the layers in the single-carrier devices are identical to those used in the working devices mentioned in our previous paragraph. From Figure 3-4(b) we can notice that the current density of the electron-only device with LiF as the only cathode

interfacial material is more than one order of magnitude greater than that of the hole-only device with a structure of ITO/PEDOT:PSS/PVK/QDs/Au. However, after inserting a Phen-NaDPO layer with the thickness of 9 nm, the current density (i.e. the electron current) of electron-only device is suppressed and, more importantly, closer to the hole current density of the hole-only device, which in turn testifies the achievement of a better charge balance in the real device due to the incorporation of 9 nm-thick Phen-NaDPO.

Meanwhile, inspired by we have discussed about the influence of WF on electron injection in chapter 3.3.2, it is highly expected that the WF of such cathode configuration (Phen-NaDPO/LiF/Al) changes because of the existence of Phen-NaDPO. Therefore, we conducted another UPS measurement on such composite cathodes. The UPS spectra of secondary-electron cut-off regions of LiF/Al and Phen-NaDPO/LiF/Al films are shown in Figure 3-4(c). By calculation, the WF of Phen-NaDPO/LiF/Al film gives a value of 3.14 eV and the WF of LiF/Al film is around 2.91 eV. From literature report we know that the lowest unoccupied molecular orbital (LUMO) level of TPBi is around 2.9-3.0 eV¹⁵³, therefore the WF of LiF/Al (2.91 eV) will cause the electrons inject spontaneously while the higher WF of the Phen-NaDPO/LiF/Al (3.14 eV) can block parts of the injected electrons, resulting in an improved charge balance and better device efficiency. Such spontaneous and restricted injections are illustrated in Figure 3-4(d). Meanwhile, the influence of WF variations are in correspondence with the demonstrated decreased current densities of single-carrier devices in the above mentioned discussions (as shown in Figure 3-4(b)). The method we applied here is similar to the reported approach by Dai and Peng et al. where poly(methyl methacrylate) (PMMA) is introduced between ZnO and QDs to reduce the electron injection for better device performance⁴¹; however, the material used in this work can also be individually acted as the interfacial layer for enhancing the electron injection and improving the device performance, which has been

successfully demonstrated in our previous discussions.

3.4 Conclusions

To have a summary, in this chapter, a cathode interfacial material Phen-NaDPO with testified electron transport behavior in organic solar cells has been transplanted and further developed in QLEDs. Compared with the reference device without using this material, better performance including the brightness, EQE, current and power efficiency are achieved concurrently in the Phen-NaDPO-based devices. What's more, the Phen-NaDPO-based device with optimized thickness demonstrates a higher EQE and CE than these of the LiF-based device while showing similar J-V characteristics. The reduced WF of the Phen-NaDPO decorated cathode based on the UPS measurement is considered to be responsible for the device improvement. Moreover, a further improvement was achieved by sequentially depositing Phen-NaDPO and LiF as the cathode interfacial layers, presenting peak EQE and CE of 8.5% and 29 cd/A, respectively. By UPS measurement and the comparisons of single-carrier devices, the improvement is attributed to a more balanced charge injection from both side due to the suppressed electron injection (almost to the same level of hole injection) by inserting this cathode interfacial material with optimized thickness.

Chapter 4 Solution-Processed Copper Oxide as Hole Injection Layer for Quantum Dot-Based Light-Emitting Diodes

4.1 Introduction

As already been highlighted in the previous chapters, due to the tunable wavelength ranging from ultraviolet to near infrared with relatively narrow full-width-at-half-maximum (FWHM)^{31, 36, 44}, quantum dot light-emitting diodes (QLEDs) have been regarded as a strong candidate for the next-generation solid state lighting and displays^{31, 36, 64, 127}. Since the first demonstration two decades ago⁴⁰, the key figure of merits, including the external quantum efficiency (EQE), maximum luminance, current efficiency (CE) of QLEDs have improved significantly, which should be attributed to the optimization of the device architecture, the technology advance on the fabrication techniques^{35, 81, 119, 131}, the choices of proper materials for charge injection and transportation^{63-65, 105} and the structural variation of the QDs^{24, 27, 102, 154}. More importantly, recent publications pointed out that the performance of QLEDs is already comparable, or even superior to other high-performance polymer/small-molecule OLEDs^{25, 41}, further proving their competence as an important alternative choice in optoelectronics.

Among the reported literatures discussing high-performance QLEDs, Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is unanimously deposited onto the indium tin oxide (ITO) electrode as the buffering layer to facilitate the hole injection to adjacent layers^{36, 41, 85}. Despite the certified high efficiency, PEDOT:PSS layer tends to etch the ITO electrode by acidic corrosion, which could lead to the device instability and degradation in terms of lifetime¹³⁹. Meanwhile, other issue like the chemically unstable nature of PEDOT:PSS compared with inorganic materials further make itself in doubt for long term use in QLEDs⁶⁵. Therefore, alternative inorganic materials for replacing PEDOT:PSS

as hole injection material have attracted significant attentions. For example, nickel oxide was applied as the hole injection/transporting layer in hybrid organic/inorganic QLED by J. M. Caruge *et al.*⁶⁵. However, the external quantum efficiency was as low as 0.18%, partially due to the rough interface between NiO and ITO resulted from the RF sputtering technique. Recently, various kinds of metal oxides, including zinc-, molybdenum-, tungsten-, rhenium-, and vanadium-oxides have been proposed as either hole or electron transport layers in OLED/QLED devices to improve the device efficiency as well as stability^{139, 155-158}. For electron injection/transportation, because of their high electron mobility, suitable energy level, stability and efficient electron injection into the active layer, zinc oxide (ZnO) nanoparticles are universally used as electron transport material in most reported QLEDs to achieve high efficiencies^{25, 36}. For hole injection, X.Y. Yang *et al.* from our group has reported the use of solution-processed tungsten oxide (WO₃) nanoparticles as hole injection layer to obtain device EQE of 3.32% and maximum luminance of 30,000 cd/m² with improved lifetime^{38, 39}. Although the performance was limited, our previous work strongly demonstrated the possibility of applying metal oxide materials as the hole injection layer in QLEDs. Therefore, to moving forward, here in this work, we shall report employing copper oxide (CuO) as a replacement for PEDOT:PSS as a hole injection layer for high performance QLEDs. This inorganic metal oxide has successfully demonstrated as the qualified hole transport layer in polymer solar cells because its work function is comparable with the highest occupied molecular orbital (HOMO) energy level of PEDOT:PSS^{159, 160}; therefore, although the working mechanisms between solar cell and LED are different, the property of CuO film can be used in the QLED architecture with suitable modifications.

In this work, a facile solution process including the spin-coating and thermal annealing of copper acetate was applied to deposit the copper oxide film on an

ITO electrode inside the nitrogen atmosphere. UPS measurement was utilized to measure the valence band maximum (VBM) of CuO with a value around 5.5 eV, which is close to the HOMO level of PEDOT:PSS. The device with CuO film as HIL presented a performance with a peak EQE over 5%, a maximum luminance over 70,000 cd/m² and a peak current efficiency of 21.3 cd/A; these numbers are as good as and even better than the performance of QLEDs based on organic HIL counterpart. To the best of our knowledge, no literature using CuO as HIL in QLED has been reported yet. And the performances of our fabricated devices are so far among the highest performance QLEDs using metal oxide as the hole injection layers up to date.

4.2 Experimental details

4.2.1 Synthesis of CdSe@ZnS/ZnS thick-shell QDs and preparation of CuO solution

Green emitting CdSe@ZnS QDs with chemical composition gradients were prepared by a modified one-pot synthesis as reported in the literature²⁶. In brief, cadmium acetate (0.14 mmol, 32.27 mg), zinc oxide (3.41 mmol, 277.60 mg) and OA (7 ml) were mixed in a 50 ml four-neck flask. The mixture was heated and degassed till 0.02 mTorr pressure for half an hour. Then, 15 ml of ODE was injected into the flask by syringe, and the whole mixture was degassed to remove the moisture brought by ODE. Then the reactor was filled with Argon and further heated to 300 °C. After maintaining the system at this temperature for 2 minutes, equivalent mole amount of selenium and sulfur (2 mmol) dissolved in TOP (2 ml) was swiftly injected into the hot mixture to form to one-pot core@shell QDs within ten minutes. And the additional shell coating was similar to that described in chapter 3.2.1.

Excess acetone and methanol was added to precipitate the QDs by centrifugation

at a speed of 7000 rpm for 10 minutes. Normally two cycles were needed to fully purifying QDs and the final precipitants were dispersed in toluene for device fabrication. The 0.1 M CuO solution was prepared by mixing copper acetate, 3 ml of 2-methoxyethanol as the solvent and 150 μ l of monoethanolamine (MEA) as stabilizer with overnight stirring at room temperature.

4.2.2 Device fabrication and characterization

The glass substrates with patterned ITO were cleaned sequentially by sonication in detergent, de-ionized water, acetone and isopropyl alcohol. The clean ITO substrates were treated with O₂-plasma for 25 minutes. The 0.1 M CuO solution was spin-deposited at 4000 rpm for 60s, followed by baking at different temperatures for 20 min in N₂-purged glove box; in order to functionalize the CuO film, the substrates with HIL were treated with UV-ozone for 10 min. PVK (Poly(9-vinylcarbazole)) (10 mg/ml) dissolved in chlorobenzene was spin-coated (3000 rpm, 60s) and thermally annealed (150 °C, 30 minutes) to form the hole transporting layer. The QD layer was formed by depositing QD solution in toluene (12.5 mg/ml) on the ITO/CuO/PVK substrate (1000 rpm, 60s) and subsequently annealed at 90 °C for 30 minutes. Then, the substrates were transferred into the thermal evaporator to deposit the electron transporting layer (TPBi) and cathode (LiF/Al) sequentially under a base pressure of 1.5×10^{-6} Torr. The effective area of the LED devices is 4 mm².

The UPS measurement was performed by applying X-Ray Photoelectron Spectroscopy (XPS) (VG Escalab 220i XL) with a He I (21.2 eV) gas discharge lamp as excitation source. AFM (Cypher S, Asylum Research) was used to characterize the CuO films. XPS measurement was performed by a homemade UHV system with monochromatic X-ray source (SPECS and Omicron electron analyzer (EA125)) with an excitation energy at $h\nu = 1286.7\text{eV}$. The current

density-luminance-voltage (J-L-V) characteristics were measured by our customized LabVIEW program based on a programmable Yokakawa GS610 source measurement unit and a PhotoResearch SpectraScan PR 705 spectrometer while the electroluminescence spectra of the QLEDs were acquired simultaneously. All measurements were carried out at room temperature under ambient conditions without device encapsulation.

4.3 Results and discussion

4.3.1 Characterization of solution-processed CuO films and CdSe@ZnS core-shell QDs

The CuO solutions prepared as described in chapter 4.2.1 were spin coated onto O₂-plasma pre-treated ITO substrates; different annealing temperatures (90, 120 and 150 °C, respectively) were applied within 20 minutes inside N₂-filled glove box. The film morphology was characterized by the atomic force microscopy (AFM) images on the CuO films spin-coated from solutions with different annealing temperatures, as shown in Figure 4-1. It can be noticed that the value of the surface roughness (quantified as the root mean square, RMS) of the films keeps rising with the increase of the annealing temperatures, with a specific value of 1.84 nm for 90 °C, 2.26 nm for 120 °C and 4.58 nm for 150 °C, respectively. As will be thoroughly discussed later in this chapter, the roughness of the CuO film surface shall play an important part in achieving high performance of the device.

Figure 4-1. Surface roughness (in RMS) of CuO thin films annealed at (a) 90 °C, (b) 120 °C and (c) 150 °C shown by AFM images.

In order to further investigate the surface properties of annealed CuO films, X-ray photoemission spectroscopy (XPS) measurement was performed. First, a full scanned spectrum of annealed CuO film was shown in Figure 4-2(a). The characteristic peaks at 530.8 eV corresponded to O 1s and 933.4 eV to Cu 2p respectively in the full spectrum strongly verified the presence of copper and oxygen within the film. It can also be noticed that additional strong peaks of In 3d, Sn 3d in the range from 400 to 600 eV are originated from the ITO coated on glass, which on the other hand demonstrating the very thin CuO films on the substrate¹⁵⁶. A enlarged XPS spectrum focusing on the Cu 2p core level was also shown in Figure 4-2(b), from which the peaks at 933.4 eV and 953.2 eV should be assigned to the Cu 2p_{3/2} and Cu 2p_{1/2}, respectively¹⁶¹. These existence of the Cu 2p_{3/2} and Cu 2p_{1/2} authenticate that copper of the film is indeed in the II oxidation state. Besides, the two shake-up peaks located at 961.4 eV and 941.5 eV, respectively further demonstrate the oxide in the sample as CuO compound¹⁶².

Figure 4-2. X-ray photoelectron spectroscopy measurements (XPS) on solution-processed CuO films: (a) Full scan (from 0 to 1000 eV); (b) High-resolution scan for Cu 2p core level region.

4.3.2 Electrical characterization and performance optimization of CuO-based QLEDs

The structure of discussed CuO-based QLED was schematically depicted in Figure 4-3(a) with a multilayer architecture in a sequence of ITO/CuO/Poly(9-vinylcarbazole) (PVK)/QDs/ 2,2',2''-(1,3,5-Benzinetriyl)-tris (1-phenyl-1-H-benzimidazole) (TPBi)/LiF/Al. Here, the CuO film is used to supplant PEDOT:PSS, which is an universal material in organic optoelectronic devices to improve hole injection^{44, 67}. Meanwhile, PVK with a thickness of 20 nm was spin coated as the hole transport layer (HTL) and TPBi with a thicknesses of 35 nm was evaporated as the electron transport layer (ETL), respectively. Figure 4-3(b) illustrates the energy level diagram of the materials utilized in this QLED; where the position of valence band energy level of CuO film was obtained based on our own measurement and calculation and the rest values of other materials were taken from reported data^{39, 116, 164, 165}. Here, in order to identify the electronic structure of CuO film, we employ the ultraviolet photoelectron spectroscopy (UPS) measurement again. Figure 4-3(c), (d) and (e) show the corresponding full-scan spectrum, secondary-electron cut-off region and valence-band region of

CuO films, respectively. According to the equation ($\text{VBM} = 21.2 \text{ eV} - (\text{E}_{\text{cutoff}} - \text{E}_{\text{onset}})$)³⁹, where 21.2 eV is the incident photon energy, the E_{cutoff} the high-binding energy cutoff from Figure 4(d) and E_{onset} the onset energy in valance-band region shown in Figure 4(e)), we can estimate the position of the valence band maximum (VBM) to be 5.48 eV. In the same way, the work function (WF) of CuO film can be simply calculated based on the equation ($\text{WF} = 21.2 - \text{E}_{\text{cutoff}}$) with a value of 5.2 eV, which is in good agreement with the reported figures^{139, 165}. Therefore, based on the measured and reported data, we can have the flat band energy band diagram; electrons are injected from the cathode to the LUMO level of TPBi and further transported to the conduction band of QDs without energy barrier while holes are injected and transported with a route of ITO/the VBM of CuO/the HOMO of PVK/the valence band of QDs. The electrons and holes will recombine radioactively inside the QDs by emitting light.

Figure 4-3. (a) Schematic structure and (b) Flat-band energy level diagram of the CuO-based QLED, respectively. UPS measurement of CuO films (annealing at 120°C) showing (c) full-scan (0 – 21.0 eV), (d) high-binding energy secondary-electron cutoff region and (e) valence-band edge region.

A list of the key figure of merits (including peak luminance, peak EQE, CE and PE) of QLEDs with CuO hole injection layers from the solutions of different annealing temperatures was shown in Table 4-1. The best device performance with peak EQE of 5.37% and maximum current efficiency of 21.3 cd/A was achieved by the device with CuO film under 120 °C annealing temperature as the HIL. Figure 4-4(a) shows the spectrum of the normalized electroluminescence (EL) from CuO-based QLED. The symmetric EL spectrum gives a Gaussian-shape emission peak with a center wavelength of 522 nm and a FWHM around 20nm. As can be observed from the current density-voltage-luminance (J-V-L) characteristics shown in Figure 4-4(b), a peak luminance over 78,000 cd/m² at the current density of 1,035 mA/cm² was obtained by the QLED with an annealing temperature of 120 °C. Due to the fact that the EL curve shows only the pure QD EL emission at the wavelength of 522 nm without the common weak emission in the blue region originated from PVK, a balanced charge injection from both sides was therefore proved: although the energy barriers encountered by holes and electrons are different, the injected electrons and holes from two electrodes recombine well; which, from another point of view, demonstrates the excellent p-type injection/transportation property of solution-processed CuO film under thermal annealing.

In order to further explicate the difference of the performance of the devices acquired under different annealing temperatures, the influences of the annealing temperatures on the workfunction (WF) of CuO films are shown in Figure 4-5(a), giving values of 5.15 eV, 5.20 eV and 5.21 eV for films annealed at 90 °C, 120 °C

and 150 °C, respectively. It has been well realized that the increase of WF of hole injection material can reduce the hole injection barrier, therefore improving the hole injection/transportation in organic electroluminescent devices¹⁶⁶. In this work, such improved hole injection as a result of the increased WF is further demonstrated by the J-V characteristics of the hole-only devices with different annealing temperatures, as shown in Figure 4-5(b). The hole-only devices has a structure of ITO/CuO (35 nm)/PVK (~100 nm)/MoO₃ (40 nm)/Al. Therefore the differences of the device performance can be explained by the comprehensive consideration of the following factors: the surface roughness (Figure 4-1), the workfunction and the influenced J-V characteristics of hole-only devices (Figure 4-5 (a)&(b)). The device with 90 °C annealing has an inferior performance because of the smaller workfunction of 90 °C annealed film with the resulted larger energy barrier and inferior hole-injection capability; On the other hand, CuO-based QLEDs with 120 °C and 150 °C annealing show comparable CuO film WFs and similar J-V characteristics from the hole-only devices while the 150 °C-annealing hole-only device exhibits fluctuation points at high applied voltages (shown in Figure 4-5(a)), which can be attributed to its higher surface roughness under high annealing temperature (Figure 4-1(c)). Similar effects have been reported previously in other structures¹⁶⁷. Therefore, taking the abovementioned factors together, the device with CuO films annealed at 120 °C achieves the best efficiency.

Annealing temperature (°C)	Max. Current Density (mA/cm ²)	Max. Luminance (cd/m ²)	Max. EQE (%)	Max. Current Efficiency (CE) (cd/A)	Max. Power Efficiency (PE) (lm/W)
90	725.5	44,650	2.74	10.0	2.29

120	1035.0	78,830	5.37	21.3	7.25
150	704.0	63,890	4.19	14.3	3.16

Table 4-1. Figure of merits for devices using CuO film as HTL under different annealing temperatures.

Figure 4-4. (a) Normalized EL spectrum and (b) current density-voltage-luminance (J-V-L) characteristics of the optimized CuO-based QLED.

Figure 4-5. (a) The secondary-electron cutoff regions from XPS measurement of CuO films deposited onto ITO substrates with different annealing temperatures. (b) Current density-voltage properties of hole-only device based on CuO films with different annealing temperatures.

4.3.3 Comparison of electrical properties and lifetime

To further certify the functionality of CuO film in QLED, a device without CuO film or other HIL with a configuration of ITO/PVK/QDs/TPBi/LiF/Al was fabricated and compared. Figure 4-6(a) shows the comparison of the electrical properties of the QLEDs with and without CuO as hole injection layer, respectively. The device without CuO film as hole injection layer presents a peak current density of 37.9 mA/cm² and maximum luminance of 6,397 cd/m², which are much worse than the performance of CuO-based device. This device comparison suggests that a thin solution-processed CuO film can significantly enhance the hole injection in such device configuration.

A further comparison was performed between the CuO-based device and a typical PEDOT:PSS-based QLED, where the device structure and the thicknesses of all the layers are identical except the optimized thickness for PEDOT:PSS. The

current density-voltage-luminance properties of CuO- and PEDOT:PSS-based QLEDs were compared in Figure 4-6(b). Both an improved current density and a higher luminance was achieved by CuO-based QLED compared with the PEDOT:PSS-based QLED. For better comparison, the key parameters of these two QLEDs are tabulated in Table 4-2. A brighter max luminance and higher power efficiency are achieved by the CuO-based QLEDs while the rest of parameters are comparable for both devices.

The device lifetime measurement was performed in order to evaluate the stability of QLEDs based on these two hole injection materials. Figure 4-7 shows the operating lifetime measurements with both devices under constant driving currents equivalent to an initial luminance of 1000 cd/m^2 . As can be seen, an improved device lifetime was achieved by CuO-based device compared with that of PEDOT:PSS-based device under same conditions. Therefore, CuO can be used as an effective alternative hole injection layer replacing PEDOT:PSS for QLED.

Figure 4-6. Current density-voltage-luminance (J-V-L) comparisons of QLEDs (a) with/without CuO and (b) with CuO and PEDOT:PSS as HILs, respectively.

Type of HIL	Max. Luminance (cd/m²)	Max. Current Density (mA/cm²)	Max. EQE (%)	Max. CE (cd/A)	Max. PE (lm/W)
CuO	78,830	1035.0	5.37	21.3	7.25
PEDOT:PSS	30,870	244.9	5.72	22.9	6.09

Table 4-2. Comparison of parameters of device performance using CuO thin film and PEDOT:PSS as HILs, respectively.

Figure 4-7. Lifetime comparison of CuO-based and PEDOT:PSS-based QLEDs. The stability tests was performed under constant applied currents corresponding to an initial luminance of 1,000 cd/m^2 for both devices without encapsulation.

4.4 Conclusions

To sum up, copper oxide (CuO)-based QLEDs with high performance have been demonstrated and characterized. A facile solution process method was applied to deposit the CuO film, and a superior hole injection capability was successfully demonstrated. The optimized CuO-based QLED presents a high EQE of 5.37% with a maximum luminance over 70,000 cd/m^2 , much higher than the performance of device without CuO film. What's more, the overall performance including the brightness, EQE, current and power efficiency are better or at least comparable to those of the PEDOT:PSS-based QLED with identical structure. Our results validate CuO as an alternative solution-processed inorganic material as a replacement for PEDOT:PSS in improving the performance and stability of quantum dot-based LEDs.

Chapter 5 Efficient Quantum Dot-Based Light-Emitting Diodes with An Inorganic Copper (I) Thiocyanate Hole Injection Layer

5.1 Introduction

In 1994, Prof. A. P. Alivisatos and his colleagues from Lawrence Berkeley laboratory and University of California at Berkeley incorporated cadmium selenide (CdSe) quantum dots (QDs) into light-emitting devices (LEDs), reporting the first quantum dot-based light-emitting diodes (QLEDs) with a relatively low external quantum efficiency (EQE) of 0.001-0.01%⁴⁰. Since then, such devices have been received extensive attentions due to the attractive characteristics such as the high photoluminescence (PL) quantum yield (QY) of QDs, tunable narrow-band wavelength from ultraviolet to infrared region, simple colloidal synthetic process and the solution processability for device fabrication^{25, 27, 36, 71}. Due to the progress in optimizing QD synthesis as well as the device configuration, significant achievements have been made during the recent years. In 2013, B. S. Mashford et al. from MIT fabricated a red QLED with a maximum EQE of 18%, presenting a device performance almost comparable to that of the state-of-the-art OLED technology²⁵. The performance of QLED with red emission was further improved by X. G. Peng et al. from Zhejiang University in 2014⁴¹. They reported a record high-performance QLED based on all-solution process with the key figure of merits, including EQE, turn-on voltage (V_{th}), power efficiency and color purity are superior or at least equivalent to OLEDs (vacuum-deposited, small molecule-, phosphorescence- or thermally activated-delayed-fluorescence (TADF)-based). Additionally, by preciously tailoring the composition of QDs and choosing the proper materials for device fabrication, P.H. Holloway and L. Qian et al. from the University of Florida fabricated a series of

RGB QLEDs, all presenting high EQEs over 10% with low V_{th} , more saturated colors and extended lifetime⁴².

To date, The reported works with record high performance have employed the normal multi-layer architecture where the active layer (QD film) is sandwiched by bottom hole injection/transporting layer and top electron transport layer; these layers (except the electrodes) are deposited by sequentially spin-coating using orthogonal solvents to keep film integrity^{26, 36, 38, 41-43, 85}. The ideal HIL/HTL materials should meet the following requirements: 1) high transparency across the full visible spectrum^{168, 169}; 2) suitable energy level for efficient hole injection and electron blocking from active QD layer^{38, 69, 131}; 3) accessible deposition technique and following post-processing conditions¹⁶⁸⁻¹⁷⁴. In term of these, as we have highlighted in the previous Chapter 4, PEDOT:PSS has been regarded as the most universal hole injection/transporting materials in QLED, OLED and organic photovoltaic (OPV) devices because of the extraordinary transparency in the visible range, the ability to form smooth surface over large areas by solution deposition, good conductivity and suitable surface work function^{27, 175-177}. Despite these advantages and certified applications in optoelectronic devices, however, PEDOT:PSS itself has certain limitations. The acidic and hygroscopic nature will influence the device performance and the hygroscopicity issue can result in device degradation⁶⁵. Another problem is that PEDOT:PSS cannot be employed as a qualified electron blocking layer due to its semi-metallic feature¹⁷⁸. All these above-mentioned shortcomings of PEDOT:PSS therefore hinder the possible commercialization of QLEDs in the future.

In order to address the issues brought by PEDOT:PSS, an alternative solution is the use of inorganic compounds, like what we have done in Chapter 4 to use CuO as the HIL to improve the device performance. Other reports have also proposed promising metal oxides such as nickel oxide, vanadium oxide, tungsten oxide, or molybdenum oxide as the HIL/HTL^{38, 39, 69, 140, 141}. These layers can be deposited

by radiofrequency sputtering¹⁰⁵, thermal evaporation under high vacuum⁷⁰ or solution process based on either the decomposition of organic-inorganic hybrid precursors or the annealing of nanoparticle suspensions^{69, 140}. Some reports revealed that metal oxide-based QLED demonstrated low efficiency due to the generated rough interface between the sputtered metal oxide layer and ITO electrode during sputtering process; On the other hand, thermal evaporation has been considered to be relatively more costly and wasteful in terms of raw materials. Therefore, the solution process is emerging as the alternative deposition method to form inorganic semiconductor. Besides the CuO we have applied as the HIL, our group also have successfully reported the use of WO₃ as the hole injection material for efficient QLED, showing the comparable device performance with PEDOT:PSS-based device in terms of luminance, quantum and current efficiencies and lifetime^{39, 69}. However, in order to form the films with suitable transparency and conductivity, metal oxide solutions normally need to be treated with high-temperature annealing¹⁴²; moreover, extra procedure like O₂-plasma treatment is necessary for some metal oxide films in order to remove the polymeric dispersing agent. Such additional requirements are contradictory to the initial purpose of using inorganic materials for replacing PEDOT:PSS.

In this chapter, we reported the utilization of solution-processed copper thiocyanate (CuSCN) film as the hole injection material in QLED. With its high transparency across the whole visible spectrum and intrinsic p-type conductivity, CuSCN, which is commercially available at low price, has been demonstrated as a qualified HTL/HIL in transistors¹⁶⁹, perovskite solar cells^{170, 174, 179}, organic/QD photovoltaic cells^{168, 171, 173, 180} and OLEDs¹⁸¹. The deposition of this material can be easily achieved by solution process or doctor blading by dissolving in suitable solvents without any further treatment. More importantly, one unique advantage should be highlighted for using CuSCN as the HIL in QLED. As we have mentioned in Chapter 2 and 3, the charge balance have been an issue in QLEDs

with normal structure: electrons are transported into QD layer spontaneously while holes suffer barriers during the injection/transportation process because the energy level difference between the valance bands of hole injection/transportation materials and QDs⁴¹. Interestingly, CuSCN has a higher hole mobility of 0.01-0.1 cm²V⁻¹S⁻¹ and a deeper valance band maximum (VBM) around 5.5 eV^{169, 170, 182}, which are both superior than PEDOT:PSS. Therefore the hole injection in CuSCN-based QLED should be more efficient and consequently, improved device performance can be reasonably expected.

5.2 Experimental section

5.2.1 Preparation of green-emitting QDs and CuSCN solutions

The preparation of CdSe@ZnS core-shell QDs were similar to our precious recipe which can be found in Chapter 3.2.1 and Chapter 4.2.1 with minor modifications^{26, 79}. The raw QD solution was purified by acetone and methanol and re-dispersed in toluene for later use. For CuSCN (Sigma-Aldrich), the as-received powder was dissolved in diethyl sulphide (DES, Sigma-Aldrich) with a concentration of 20 mg/ml with overnight stirring inside the glovebox. The solutions were filtered before use.

5.2.2 Device fabrication and characterization

The cleaning process for glass substrates with patterned ITO is identical to our previous description with a sequence of ITO detergent, de-ionized water, acetone and isopropyl alcohol. For device fabrication, first of all, a HIL was deposited on top of ITO. For PEDOT:PSS (Clevios P VP Al 4083), the solution was filtered by 0.45 µm PVDF filter and then spin-coated onto ITO (4000 rpm, 60 s) and baked at 140 °C for 20 min. The CuSCN film was spin-coated with a speed of 2000 rpm for 60s and further annealed at a temperature of 120 °C for 20 min. PVK (Sigma-Aldrich, 10 mg/ml dissolved in chlorobenzene) and QD solutions (10 mg/ml in toluene) were spin-coated with optimized speeds (3000 rpm and

1000 rpm) and annealing temperature (both 20 mins), respectively. Then, the electron transporting layer (TPBi) and cathode (LiF/Al) were thermally evaporated in sequence under a base pressure of $\sim 1.0 \times 10^{-6}$ torr. The effective area of QLED is $2 \times 2 \text{ mm}^2$, defined by the overlapped area of ITO and Al electrodes.

Surface roughness measurement was performed by using AFM (Cypher S, Asylum Research). The powder XRD measurement was performed by Shimadzu XRD-6000 with Cu-K α radiation operated at 40 kV and 30 mA and a scintillation counter scintillator as detector. A Shimadzu RF-5301PC spectrofluorophotometer and a Shimadzu UV-1800 spectrophotometer were used to obtain the photoluminescence and absorption spectra of QD solutions, respectively. The electrical properties of devices in this work were measured by customized program by using a programmable Yogakawa GS610 source measurement unit and a spectrometer (PhotoResearch SpectraScan PR 705) with the electroluminescence (EL) spectra acquired simultaneously. All measurements were carried out at room temperature under ambient conditions without encapsulation.

5.3 Results and discussion

5.3.1 Film characterization and comparison

The schematic diagram of device configuration is shown in Figure 5-1(a), with a structure of, in the following order, indium tin oxide (ITO), a PEDOT:PSS or CuSCN as HIL (40 nm), poly(9-vinylcarbazole) (PVK, 40 nm) as HTL, CdSe@ZnS core-shell QDs (40 nm), TPBi with a thickness of 35 nm as ETL, lithium fluoride (LiF, 1 nm) and aluminum (Al, 100 nm). Figure 5-1(b) shows the energy level diagram of the materials used in QLED with these values taken from reported literatures^{26, 69, 168}. The valance band maximum (VBM) of CuSCN is around 5.5 eV, which is deeper than the highest occupied molecular orbital

(HOMO) level of PEDOT:PSS. Therefore, as we discussed in the introduction part, such deep VBM is supposed to have a profound effect on device performance.

Figure 5-1. (a) Schematic illustration of QLED structure and (b) Flat-band energy level diagram of materials of QLEDs.

First of all, it is necessary to compare the structural and optical properties of CuSCN and PEDOT:PSS films. The atomic force microscopy (AFM) measurement in Figure 5-2 shows the topographic images of (a) ITO, (b) ITO/PEDOT:PSS and (c) ITO/CuSCN deposited onto the glass substrates, respectively. The surface roughness of pure ITO film has a RMS (root mean square) value of 0.976 nm. And the surface roughness was slightly increased to a RMS value of 1.966 nm with a smooth morphology after PEDOT:PSS was spin-coated onto the ITO substrate. Meanwhile, the RMS value for the CuSCN film coated on the ITO substrate has a slightly higher RMS value with 4.745 nm; these values are in good correspondence with the reported measurement results¹⁷³. Therefore it is clear to clarify that the AFM measurements demonstrate the successful fabrication of CuSCN film forming onto the ITO/glass substrates with solution process although further optimization might be in demand.

Figure 5-2. AFM topography images of (a) ITO, (b) PEDOT:PSS and (c) CuSCN films deposited onto glass substrates, respectively.

The x-ray diffraction (XRD) analysis was conducted to investigate the crystallinity of CuSCN. Figure 5-3(a) shows the XRD pattern for the as-purchased CuSCN powder, demonstrating a dominant orthorhombic α -phase, which is consistent with the literature report¹⁸². However, our XRD measurement cannot observe the crystallinity of the CuSCN films (data not shown), which could be ascribed to the small film thickness¹⁶⁹. In this work, the target QLED occupies a bottom-anode, bottom-emitting LED architecture; therefore it is also of great importance to compare the optical transmittance of these two HIL materials, CuSCN and PEDOT:PSS, which makes the optical transparency measurement necessary. Figure 5-3(b) shows the comparison of absorption spectra (in the range of 350-700 nm) of CuSCN (red) and PEDOT:PSS (black) thin films with identical thickness spin-coated on glass substrates. The red curve shows that CuSCN exhibits high transparency in the wavelength above 500 nm and a slight tendency to increase in the short wavelength region due to its wide optical bandgap (> 3.5 eV). For PEDOT:PSS film, it tends to have less absorption in the short-wavelength region but absorbs more beyond 550 nm to the longer-wavelength region. Such optical characteristic of PEDOT:PSS should be attributed to the intragap absorption originated from the polaronic changes due to the introduced oxidative doping for improving its conductivity¹⁸¹.

Figure 5-3. (a) X-ray diffraction analysis of the CuSCN powder with a dominant α -phase of the sample; (b) Comparison of the absorption spectra from PEDOT:PSS and CuSCN films spin-coated on glass substrates with the same thickness (45 nm). Inset: Ultraviolet-visible absorption and photoluminance spectra of QD solutions.

5.3.2 Photoluminance vs. electroluminescence of CuSCN-based QLED

To further confirm the suitability of CuSCN film as HIL in QLEDs, two sets of devices with PEDOT:PSS and CuSCN as HILs were fabricated with a spin-coated green-emitting QD film as the active layer. The inset of Figure 5-3 shows the photoluminance (excited by 325 nm source) and the ultraviolet-visible absorption spectra of QD solutions (dissolved in toluene). Further the PL spectrum of QD was compared with the normalized electroluminescence (EL) spectra of the QLEDs based on CuSCN and PEDOT:PSS HILs acquired at an applied voltage of 5V, as shown in Figure 5-4(a), respectively. It can be clearly observed that the PL spectrum of QD solution and the EL spectra of QLEDs overlapped identically, presenting a Gaussian shape emission curve with peak wavelength at 528 nm and a FWHM of 20 nm. Moreover, the EL spectra evolution of CuSCN-based device under different applied voltages from 5 V to 7.5 V is displayed in Figure 5-4(b), showing that the EL spectra were not red-shifted with increasing voltages but identical to the PL emission of QD solution. Such perfect overlap between the EL and PL together with the stable EL spectra evolution under applied voltages of CuSCN-based device prove that CuSCN is capable to afford efficient hole injection and stable to maintain a reliable recombination zone.

5.3.3 Device performance comparison

Figure 5-4(c) shows the current density-voltage-luminance (J-V-L) characteristics of CuSCN- and PEDOT:PSS-based QLEDs, respectively. The workfunction of PEDOT:PSS has a reported value of 4.9-5.2 eV^{41, 69}; Compared with the HOMO level of PVK (5.8 eV), there exists an energy barrier of 0.6-0.9 eV between the adjacent layers, which should be detrimental to the hole injection. Such a noteworthy barrier can be reflected by the high turn-on voltage (V_{th}) with a value of 4.2 V (defining at a luminance of 1 cd/m²); On the other hand, the turn-on voltage of CuSCN-based QLED decreases significantly by 0.8 volt to 3.4 V.

Such a reduction in turn-on voltage should be attributed to the reduced energy barrier for hole injection, which can be resulted from the deeper VBM of CuSCN (5.5 eV); the improvement in V_{th} is in good agreement with our expectation as well as other reports¹⁶⁹. The comparisons of the external quantum efficiency (EQE) and current efficiency (CE) as two functions of the current density (CE-J) characteristics for the CuSCN- and PEDOT:PSS-based QLEDs with the optimized device configuration, respectively are shown in figure 5-4(d) and (e). The figure of merits of CuSCN- and PEDOT:PSS-based devices are tabulated in Table 5-1 for comparison. To be specific, our best performing QLED based on CuSCN yields a maximum brightness of 140,000 cd/m^2 , a maximum current efficiency of 28.4 cd/A with an EQE of 6.9%, which are fully comparable with PEDOT:PSS-based QLED.

Figure 5-4. Comparison of device performance for CuSCN and PEDOT:PSS HIL QLEDs. (a) Normalized EL spectra of QLEDs based on CuSCN and PEDOT:PSS HIL compared with QD PL spectra; (b) EL spectrum evolution under different applied voltages for CuSCN-based QLED; (c) Current density-voltage-luminance (J-V-L) characteristics for CuSCN and

PEDOT:PSS-based QLEDs; (d) External quantum efficiency (EQE) of CuSCN and PEDOT:PSS-based QLEDs as a function of current density; (e) Current efficiency (CE) versus current density characteristics for both devices; (f) Electrical measurements on the current density-voltage curves for the hole only devices based on CuSCN and PEDOT:PSS, respectively.

Type of HIL	Turn-on Voltage [V] @ 1cd m ⁻²	Max. Luminance [cd m ⁻²]	Max. Current efficiency [cd A ⁻¹]	Max. EQE [%]
PEDOT:PSS	4.2	151,400	26.5	6.6
CuSCN	3.4	146,700	28.4	6.9

Table 5-1. Comparison of key parameters of QLEDs with PEDOT:PSS and CuSCN as HILs, respectively.

5.3.4 Electrical properties of hole-only devices based on CuSCN and PEDOT:PSS

As been highlighted in the introduction part, one of the most inspiring advantages regarding the use of CuSCN as HIL is the improved capability of injecting holes in QD-based device due to the deeper VBM as the hole injection level and the proved high hole mobility¹⁷³. In this work, to demonstrate this from another perspective, two sets of hole-only devices are fabricated with a multilayer structure of ITO/HIL/PVK (40 nm)/QDs (40 nm)/Au (100 nm), one with CuSCN and the other with PEDOT:PSS as the HIL, respectively while the thickness of the other layers keeps the same. Figure 5-4(f) gives the electrical characteristics (voltage vs. current density) of both single-carrier devices, clearly showing that the current density of CuSCN-based hole-only device is almost one order of magnitude higher than the that of the PEDOT:PSS-based device. It should be

mentioned that in such configuration for hole-only devices, the current will solely represent the behavior of hole transport because the electrons are totally blocked by the PVK layer. Due to the fact that there are no difference in these two hole-only devices except the choice of HIL, we can attribute the improved hole current to the utilization of CuSCN as a replacement for PEDOT:PSS.

5.4 Conclusions

In summary, we reported the successful application of a solution-processed CuSCN film which can be spin-coated as the HIL for high performance QLEDs. Due to its suitable optical transparency, desirable energy level and high hole mobility, CuSCN reduces the turn-on voltage of QLED by 0.8 volt while achieving better or at least comparable performance relative to the control device based on PEDOT:PSS. The resulted device presents a maximum luminance exceeding $140,000 \text{ cd/m}^2$ with peak current efficiency over 28 cd/A . Such performance is attributed to effective hole injection, reduced energy barrier and better charge balance resulted from CuSCN. To the best of our knowledge, this work is the first attempt using this material as the efficient HIL in quantum dot-based LEDs. Comparing the performance of CuSCN-based QLED with CuO-based QLED, a lower turn-on voltage, higher maximum luminance and EQE has been achieved. What's more, as a relatively cheap and commercially-available material, we believe CuSCN can further act as an ideal inorganic hole injection candidate for the fabrication of other inorganic or tandem QLEDs with proper optimization.

Chapter 6 High-Performance All-Inorganic Quantum Dot-Based Light-Emitting Diodes

6.1 Introduction

In recent years, thin-film light-emitting diodes based on colloidal quantum dots (QDs) as emitter are showing comparable performance with organic LEDs in terms of device efficiency, colour purity and lifetime; the extraordinary characteristics of QLED including the cost-effective processability, the compatibility with existing technology and purer colour rendering, proves itself as an optimistic candidate for full-colour light source of display and lighting applications^{25, 26, 33, 41, 42}. Among the reported QLEDs with high performance, we can find that organic materials are universally utilized as the charge transporting materials to realize the expected efficiency. Therefore here comes the problem: although such mature choices can contribute to the best efficiency, organic materials tend to present weakly stable characteristics compared with the inorganic materials, showing a tendency of degradation under high current densities, which has been discussed and demonstrated in our previous chapters¹⁸³.

Therefore, if QLED really wants its commercialization in the market as the light source for solid state lighting and for backlights for televisions, its stability will be one of the biggest issues⁴⁴. Researchers have proposed to fabricate QLED with inorganic materials to improve the device stability. However, although an improved device stability could be realized, the overall performance was left far behind that of the QLED based on organic materials. For example, J. M. Caruge from MIT reported inorganic QLED with sputtered metal oxides, giving a peak brightness of only 1,950 Cd/m² and an EQE less than 0.1%¹⁰⁵; V. Wood et al. from the same group improved the device efficiency to 0.2% by investigating the electronic and structural characteristics of the inorganic films¹³¹. To the best of our knowledge, such luminance and efficiency are the reported highest values for

inorganic QLED so far. Two possible explanations are considered to be responsible for such inferior device performance: one is the imbalanced charge injection originated from the large energy barrier existed between the p-type metal oxide and QDs; second reason is that the inorganic metal oxide films have the strong quenching effects on the neighbouring QD emissive layer (which is also known as QD charging effect)^{105, 184, 185}.

Therefore, problems regarding to the charge imbalance and QD charging of inorganic QLED should be solved in order to achieve high-efficiency QLEDs. However, if we consider the transparency, conductivity and processability issues, compared with the widely-used organic semiconductors such as PEDOT:PSS, PVK or TFB as charge transporting materials, limited options are existed in the area of inorganic materials in fabricating all in-organic QLEDs. Previous reports applied radio-frequency (RF) sputtering technique to deposit metal oxides, resulting in a rough film surface and damaged underlying layers, which should account for the device low efficiency^{105, 131}. Accordingly, solution process by spin coating emerges as the alternative choice for film deposition because of its better compatibility with the deposition of active layer and improved morphology and controllability^{26, 36, 39, 69, 85}. For example, ZnO nanoparticles have been spin-coated as the electron transporting layer on QD films in the reports with the recorded performance QLEDs emitting the three primary colours^{33, 41-43}. Dai et al. creatively applied an insulating material deposited between QD layer and ZnO film to modulate the charge balance and inhibit the QD charging, achieving the best QLED performance so far⁴¹. Therefore, based on the aforementioned works and technologies, all-inorganic QLEDs with better device performance could be achieved by the combination of optimized film deposition technique and device architecture.

In this work, all-inorganic QLEDs with high performance are achieved by using metal oxide films as charge injection/transporting layers and an inorganic

material as the insulating layer between QD layer and adjacent metal oxide layers. This insulating layer is of great importance in alleviating the side effects from the use of metal oxide films. By precise modulation and optimization, our all-inorganic QLED shows the best efficiency with a peak brightness over 7,600 cd m⁻² and an EQE of 1.74%, respectively. To the best of our knowledge, such performance is among the reported highest QLEDs comprising of all inorganic materials up to date.

6.2 Experimental details

6.2.1 Preparation of QDs and ZnO nanoparticles

A modified one-pot synthesis was applied to grow the CdSe@ZnS core@shell QDs with gradient chemical composition^{35, 42, 79}. Typically, a mixture of cadmium oxide (CdO, 0.1 mmol), zinc acetate (Zn(Ac)₂, 4 mmol) and 5 mL of oleic acid (OA) in a 50 ml four-neck flask were degassed and heated to 120 °C simultaneously till transparent solution was formed. Next, 1-octadecene (1-ODE) with a volume of 15 ml was injected into the flask with further degassing and heating to the previous temperature and pressure. Further, the mixture was filled with inert gas and swiftly heated to 310 °C with intense stirring. The prepared syringe containing a mixture of tri-n-octylphosphine (TOP, 1.6 ml) with selenium (Se, 0.15 mmol) and sulphur (S, 4 mmol) was inserted into the flask by swiftly injection; a duration of 10 minutes with this high temperature was needed to form the core@shell QD structure. The purification procedure is identical to our previous descriptions (Chapter 3). As an orthogonal solvent, toluene was used to dissolve synthesized CdSe@ZnS and CdSe/CdS/ZnS QDs for the subsequent spin coating of films.

A reported sol-gel method was used to synthesize ZnO nanoparticles with monodispersity and size uniformity⁸⁵. A solution of tetramethylammonium hydroxide (TMAH) in ethanol (0.5M, 10 mL) was drop-wisely injected into a 30

ml dimethyl sulfoxide (DMSO) dissolved with zinc acetate (0.1M). The mixture was under vigorous stirring for 2 hours under ambient conditions. For the purification, acetone was added to precipitate the ZnO nanoparticles and purified ZnO powder was dissolved in ethanol with a concentration of 25 mg/ml for spin coating.

6.2.2 Fabrication of QLED devices

ITO detergent, de-ionized water (DI-water), acetone, and isopropyl alcohol (IPA) were sequentially applied to clean the customized patterned ITO substrates by sonication. The substrates then received the O₂-plasma treatment in order to increase its WF as well as improving the hydrophilic property. For the metal oxide deposition, first, the MoO₃ film as HIL was formed by spin coating onto the ITO substrate (6000 rpm, 60 s) and annealed at 150 °C for 15 minutes according to the literature¹⁸⁶. An additional O₂-plasma is necessary to remove polymeric dispersing agent and functionalize the MoO₃ film. Next, NiO film as the hole transporting layer was spin coated on the MoO₃ film (4000 rpm, 60 s) by thermal decomposition of a stoichiometric complex of including MEA and Ni²⁺ with the equivalent mole ratio and further received an annealing temperature of 275 °C for 30 min¹⁴⁰. The QD film as the active layer was deposited as our previous conditions with a speed of 1000 rpm for 1 minute and further annealed at a temperature of 90 °C for 20 minutes inside the glovebox. For the electron transporting layer, ZnO nanoparticles dissolved in ethanol was spin coated on the QD layer with a speed of 2000 rpm for 60s and further annealing at 90 °C. Then the samples were transferred into the evaporator chamber for cathode deposition (Al, 100 nm) under a base pressure of The multilayer substrates were then loaded into thermal evaporator and the Al cathode with a thickness of 100 nm was thermally deposited under a base pressure of $\sim 1.0 \times 10^{-6}$ Torr.

6.2.3 Instrumentation

The electrical properties of devices in this work were measured by customized program by using a programmable Yokakawa GS610 source measurement unit and a spectrometer (PhotoResearch SpectraScan PR 705) with the electroluminescence (EL) spectra acquired simultaneously. The EL intensity from the active area of the substrate (2 mm by 2 mm) was first obtained in the form of photon current by the measurement of an un-mounted photodiode which was placed in contact with the active area. Then the performance of device (luminance, EQE, CE, PE, etc.) were calculated automatically by the above-measured data. The surface roughness measurement was performed by using atomic force microscopy (Cypher S, Asylum Research) to characterize the metal oxide films (MoO_3 , NiO and ZnO). Energy-dispersive spectroscopy (EDS) on field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7610F) was applied to perform the element mapping. All measurements were carried out at room temperature under ambient atmosphere.

6.3 Results and discussion

6.3.1 Device structure and electrical characteristics

The proposed QLED with all inorganic compositions has a similar structure with our work in this thesis, giving a multilayer architecture with ITO substrate (anode)/ MoO_3 /NiO/QDs/ZnO/Al(cathode) as shown in Figure 6-1(a). The MoO_3 thin film acting as the hole injection layer was spin coated from the MoO_3 NPs dissolved in xylene; and the hole transporting layer was deposited from the thermal decomposition of the coordination complex (Ni^{2+} and monoethanolamine) to form NiO film. The green emitting CdSe@ZnS core-shell QDs were deposited sequentially as the emissive layer and ZnO layer formed by spin-coating ZnO NPs in ethanol were chosen as the electron transporting layer. Therefore in such device configuration, all functional films

except the Al cathode were deposited continuously using the solution process. It can be expected to fabricate QLED with all-solution process using some kind of “liquid” electrodes. The image shown in Figure 6-1(b) demonstrates the NTU logo with bright and saturated green emission by using the QLED structure shown in Figure 6-1(a).

Figure 6-1(c) shows the flat band energy diagram of our proposed QLED. It can be observed that a charge imbalance exists in such structure: the electrons are transported from the Al cathode to the conduction band of QD by the aligned energy band of ZnO layer; however, on the other hand, the hole injection is much more difficult: A carrier breakthrough exists at the MoO₃/NiO interface due to the deep lying electronic states of n-doped MoO₃ (the electrons are extracted from the valence band of NiO through the conduction band of MoO₃). Therefore, in such prototypical QLED, electrons are much easier to be injected into the active layer than holes because of the different energy barriers they encountered.

The normalized EL spectrum of our QLED is displayed in Figure 6-1(d). This EL curve shows a typical QD emission with a centre wavelength at 508 nm and a FWHM of 35 nm, demonstrating the efficient and stable recombination zone inside the device for electrons and holes to recombine radioactively. Figure 6-1(e) shows the characteristic of applied voltage vs. current density vs. luminance (J-V-L) curves of the QLED measured with our customized experimental setups as described in Instrumentation section. This device presents a peak brightness of 5,200 cd/m² and a turn-on voltage (V_T) as low as 3 V, which suggests the relative injection capability of these metal oxides in this device configuration. Figure 6-1(f) shows the relationship of the EQE and CE as functions of current density of this QLED, presenting a maximum EQE of 1.22 % and a CE of 3.37 cd/A. Compared with the J. M. Caruge’s & V. Wood’s work regarding to all-inorganic material with the highest performance (peak brightness of 1950 cd/m² and peak EQE of 0.2%), our attempt provides much better efficiencies, which on the other

hand demonstrates the feasibility of such solution-processed metal oxide films as the efficient charge injection/transporting materials in inorganic QLED.

Figure 6-1. (a) Schematic device structure of inorganic QLED with solution process (ITO/MoO₃/NiO/QDs/ZnO/Al); (b) The image showing a working QLED under applied voltage of 6V; (c) The corresponding flat-band energy diagram of QLED; (d) Normalized EL spectra of all-inorganic QLED; (e) Current density-voltage-luminance (J-V-L) characteristics and (f) external quantum efficiency and current efficiency as functions of current density (EQE-CE-J) characteristics of all-inorganic QLED, respectively.

6.3.2 Device optimization for achieving high performance

As we mentioned several times in the previous chapters, charge balance is always an important issue in achieving high-performance QLEDs. ZnO nanoparticles have been the most successful electron transporting material for the reported QLEDs with the best efficiency not only in the visible range but also extended to UV and near infrared regions^{41-43, 138}. However, due to the perfectly matched conduction band of ZnO to the WF of cathode and to the CB of QDs as well, an excess electron injection often takes place in the working QLED compared with the confined hole injection which should be ascribed to the energy barrier. What's

more, it has been testified that metal oxides often trend to quench the QD emission by the ultrafast non-radiative process of inefficient trion emission, which depends on the proximity of emitters to the interface^{105, 187}. Researchers have proposed to weaken such quenching effect by isolate them. For example, X. G. Peng et al. use organic poly(methyl methacrylate) (PMMA) with optimized thickness to modulate not only the charge balance but also the charging effect, resulting in best device performance. Inspired by their report, in this work, we inserted an inorganic material (LiF) with very thin thickness (0.6 nm) between ZnO and QD to achieve the same function. Since the thickness of LiF is too thin to form a continuous film and its CB is close to that of ZnO, electrons can still be injected into the QD layer by both direct injection and tunnelling process. In order to assess the effect of LiF deposition, first we compare the morphology of QD films before and after the deposition of LiF, as shown in Figure 6-2(a)&(b). It can be observed that the surface morphology of the QD films keeps identical.

Figure 6-2. AFM images of the QD films with and without LiF deposition. (a) QD film deposited on NiO/MoO₃/ITO and (b) LiF thin layer covered QD film deposited on NiO/MoO₃/ITO.

Further, the current density-voltage-luminance (J-V-L) performance of the new device (QLED II) is evaluated, as shown in Figure 6-3 (a). The device presents a peak brightness of 7,600 cd/m², which is a 1.5-fold improvement than that of

QLED I (5200 cd/m^2). The EQE-CE-J relationship shown in Figure 6-3(b) presents a max EQE of 1.74% with a peak CE of 4.79 cd/A , which are 1.4 times higher than those of the QLED I without LiF. In order to investigate the dynamic process of the QD film under different surroundings, we applied the time-resolved photoluminescence (TRPL) spectroscopy measurement and the results are shown in Figure 6-3(c). By fitting the original decay curves from the measurement, we can get the PL lifetime of the QD films. It can be noticed that after depositing ZnO film on top of QD film, the PL lifetime of QDs decreased from 13.70 ns to 11.97 ns, which should be attributed to the inefficient triion emissions caused by the quantum dot charging effect. On the other hand, after the insertion of thin LiF film between QD and ZnO films, the average PL lifetime of QD film is recovered to 12.85 ns. The recovery of PL lifetime indicates that such insertion of insulating material with thin thickness can contribute to the charge neutrality as well as the luminous integrity of the QD active layer in the working device, which are in good correspondence with the previous literature⁴¹.

Figure 6-3. (a) Current density and luminance as functions of bias voltage of the second device.

Inset shows the schematic diagram for the charge injection into QD layer; (b) EQE-J-CE relationship of the QLED in log-log scale; (c) Time-resolved photoluminescence (TRPL) spectroscopy measurement on QDs, ZnO/QDs and ZnO/LiF/QDs films, respectively.

6.3.3 Numerical simulations on inorganic QLEDs

In order to understand the underlying physics for the QLEDs discussed in this work, we performed the numerical simulations using a commercial APSYS package with material parameters properly configured¹⁸⁸. The simulation is able to self-consistently solve the Poisson and Schrödinger equations under proper boundary conditions. Meanwhile, the intra-band tunnelling and the thermionic emission from the carrier transport at each heterojunction are also taken into consideration. Table 6-1 illustrates the physical parameters of the materials in QLED I & II. To be specific, the band gap of the NiO ranges from 3.6 eV to 4.0 eV depending on the different fabrication technologies, and in our case, we set it to 3.76 eV^{189, 190}. The ratio between the conduction band offset and the valance band offset of the CdSe@ZnS core-shell system is 70:30¹⁹¹, while the electron affinity for ZnS is 3.2 eV below the vacuum energy level¹⁹². Thus, by using the energy band gaps shown in Table 6-1 for the CdSe@ZnS core-shell system, the electron affinity for the CdSe material is calculated to be 4.6 eV. A stack of three-period quantum dots has been chosen to enable the light emission from the studied devices, named (CdSe@ZnS)₃ in the following discussion. However, it should be mentioned that due to the complexity of spin coating the QD solution into films during the experiment, it is hardly to obtain the exactly same films as the assumed conditions in the simulation.

Two QLEDs (QLED I & QLED II) with different device architectures were numerically constructed in this work. For both devices, A 40 nm thick MoO₃ layer and 5 nm NiO layer were chosen as the HTL while the 40-nm thick ZnO film as the ETL. The three-period CdSe@ZnS core-shell systems were embedded between the HTL and the ETL to produce the electron-hole pairs, with the thicknesses of 3 nm and 2 nm for cores and shells, respectively. As we have assumed in the previous part, a thin LiF layer is beneficial in balancing the

charges by modulating the electron injection, which will also be demonstrated and discussed thereafter.

Material	Band gap (eV)	Electron affinity (eV)	Thickness (nm)
MoO ₃	2.9 ¹⁹³	2.3 ¹⁹³	40
NiO	3.76 ¹⁸⁹	1.46 ¹⁹⁴	5
CdSe	1.74 ¹⁹¹	4.6 (by calculation)	3
ZnS	3.81 ¹⁹¹	3.2 ¹⁹²	2
LiF	13.6 ¹⁹⁵	3.1 ¹⁹⁶	0.6
ZnO	3.2 ¹⁹⁷	4.32 ¹⁹⁸	40

Table 6-1. Material parameters used in the numerical calculations.

Figure 6-4. Energy band diagrams at the equilibrium state for (a) QLED I of MoO₃/NiO/(CdSe@ZnS)₃ QDs/ZnO architecture and (b) QLED II of MoO₃/NiO/(CdSe@ZnS)₃ QDs/LiF/ZnO architecture (E_C , E_V and E_F represent for the conduction band, valence band and Fermi level, respectively.)

Figure 6-5. Energy band diagrams at 40 V for (a) QLED I of $\text{MoO}_3/\text{NiO}/(\text{CdSe@ZnS})_3$ QDs/ZnO and (b) QD-LED II of $\text{MoO}_3/\text{NiO}/(\text{CdSe@ZnS})_3$ QDs/LiF/ZnO architecture with LiF (E_C , E_V , E_{FE} and E_{FH} represent conduction band, valence band and quasi-Fermi level for electrons and hole, respectively.)

Figure 6-4(a) & (b) shows the numerically calculated energy band diagrams at the equilibrium state for QLED I and QLED II, respectively. The energy band alignments for QLED I and QLED II are in consistence with the parameters demonstrated in Table 6-1. The energy bands under a fixed applied voltage for both QLEDs are illustrated in Figure 6-5(a) & (b), respectively. The electron concentration in the CdSe@ZnS QDs that are shown in Figure 6-6 can be obtained according to the alignments of the E_C , E_V , E_{FE} and E_{FH} in Figure 6-5(a) & (b). It can be clearly seen that the electron concentration in the CdSe@ZnS quantum dot region for QLED II is higher than that for QLED I. Since the structure of both devices are identical except the additional LiF layer, the increase of the electron concentration in the CdSe@ZnS quantum dot regions for QLED II should be ascribed to the thin LiF. Due to the more balanced charge injection, QLED II demonstrates an obvious improvement in device performance in peak brightness, EQE, CE, etc., as shown in Figure 6-3(a) & (b). What's more, the reduced charger transfer into the ZnO layer for QLED II well explains the increased lifetime in Figure 6-3(c). In addition, we also calculated the different hole injections for QLED I and QLED II, which are shown in Figure 6-7. It is

clearly to see that due to the thin LiF layer between QD and ZnO films, the hole injection efficiency has been greatly enhanced compared to that of QLED I, which, together with the modulated electron concentration as shown in Figure 6-6, should be responsible for the improved device performance including luminance, EQE and CE for QLED II as demonstrated in Figure 6-3(a) & (b).

Figure 6-6. Numerically calculated electron concentration profiles in the CdSe@ZnS core-shell regions for QLED I of MoO₃/NiO/(CdSe@ZnS)₃ QDs/ZnO and QLED II of MoO₃/NiO/(CdSe@ZnS)₃ QDs/LiF/ZnO at 40 V.

Device	Max. Luminance (cd/m ²)	Max. EQE (%)	Max. CE (cd/A)
Our device (QLED II)	7,600	1.74	4.79
QLED (NiO) ¹⁰⁵	1,950	<0.1	0.064
QLED (WO ₃ /NiO) ¹³¹	N/A	0.2	N/A

Table 6-2. Device key performance comparison of our inorganic QLED with other high-performance QLEDs.

Figure 6-7. Numerically calculated hole concentration profiles in the CdSe@ZnS core-shell regions for QLED I of MoO₃ QDs/NiO/(CdSe@ZnS)₃/ZnO and QLED II of MoO₃/NiO/(CdSe@ZnS)₃ QDs/LiF/ZnO at 40 V.

6.4 Conclusion

In conclusion, we have demonstrated all-inorganic QLEDs with record high electroluminescence efficiency and peak luminance as tabulated in Table 6-2. The superior performance was achieved by the use of solution-processed metal-oxide films compatible with QDs deposition and the delicate design of device architecture with the insertion of LiF insulating layer between QDs and adjacent electron transport layer. The results and analysis mentioned in this work suggest that the interfacial engineering is quite critical in order to improve device performance. Therefore, we strongly believe that the method demonstrated here could make contributions to the realization of all-inorganic QLEDs with higher performance and multicolour emission in the future.

Chapter 7 Conclusions and Future Works

7.1 Conclusions

As a promising candidate for next-generation lighting and display technologies, quantum dots and QLEDs are receiving more and more attention in the recent years due to their unique and excellent characteristics including the size-dependent controllable emission wavelength, high quantum yield, high colour purity (due to narrow emission bandwidth), wide colour gamut and solution-based synthesis and fabrication processability^{25, 27, 36, 40, 44, 102, 199}. Here, in this thesis, we discussed the inadequacy of current high-performance QLEDs in terms of the use of organic charge transport materials, the resulted device instability and unbalanced charge injection and further gave the alternative solutions to the aforementioned shortcomings. We hope that the work from this dissertation can contribute not only to the academic research but also to the industrial prototyping and even for the full commercialization in the near future.

First, we attempted to improve the charge balance in the working QLED by inserting a substituted cathode interfacial layer in order to decrease the overflowed electron current. We successfully demonstrated that the introduced interfacial material (Phen-NaDPO) can replace the commonly used LiF to decorate the cathode, resulting in an optimized device with decent device performance with an maximum EQE of 7.4% and a current efficiency over 24 cd/A; What's more, the combination of Phen-NaDPO and LiF as a bilayer for cathode buffering can further improve the device performance with a peak EQE of 8.5% and a CE over 29 cd/A. Incorporating the organic CIM led to a more balanced electron/hole injection from both electrodes and thus enhanced device performance, which has been testified by our analysis based on the UPS measurements and the electrical measurement of single-carrier devices.

Moreover, aiming to solve the problems related with the use of PEDOT:PSS as the HIL of QLEDs, we proposed and testified two possible candidates: solution-processed copper oxide (CuO) and commercially-available copper thiocyanate (CuSCN) as the replacements. For CuO-based QLED, the optimized one presents a comparable and even higher device performance with PEDOT:PSS-based QLED, showing a maximum EQE of 5.4% with a high brightness over 70,000 cd/m^2 , which were among the highest values of QLED using inorganic metal oxide as the HIL at that time. What's more, we discussed the effect of the annealing temperature on the CuO film formation and its further influence on the device performance. Moreover, we demonstrated that the device operation lifetime was greatly improved by substituting PEDOT:PSS with solution-processed CuO film.

Meanwhile, as an inorganic cost-effective material, CuSCN, which has been demonstrated as a qualified hole transporting material in perovskite solar cell, organic LED and QD solar cells, attracts our attention due to its excellent optical and electrical properties. For the first time, we successfully demonstrated its application as a replacement of PEDOT:PSS in improving the performance of QLED, giving a high EQE of 6.9% with a maximum luminance of 140,000 cd/m^2 . The use of CuSCN in QLED has a unique advantage in improving the charge balance of the device by increasing the hole injection current; therefore the turn-on voltage of CuSCN-based QLED was dramatically reduced by 0.8 volt compared with that of PEDOT:PSS-based ones. We believe CuSCN can further act as an ideal inorganic hole injection candidate for all-inorganic or tandem QLEDs.

Last but not the least, to avoid the negative influence from the organic materials used in popular high-performance QLED, we developed the universal all-inorganic QLED architecture. Our inorganic QLED with green emission applied solution-processed metal oxide films as both hole and electron

injection/transporting layers, showing the maximum brightness and quantum efficiency with values of 7,600 cd m⁻² and 1.74%, respectively, 4-fold higher than the QLED I's luminance value and 9-fold higher than the QLED I's efficiency value. We highlighted the insertion of LiF as the buffering layer to optimize charge balance and, more importantly, to reduce the quenching effects of inorganic metal oxide on QD emission. To the best of our knowledge, this study is the first report regarding to high-performance, all-inorganic QLEDs by discussing insightfully into the performance enhancement of inorganic electroluminescent devices. This work suggests that the interfacial engineering is quite critical for improving the performance of inorganic QLED; we anticipate that our results presented in this thesis will be a starting point for achieving all-inorganic QLEDs with multicolour emission by interfacial optimization and modification.

7.2 Perspectives for future work

Although the performance of QLEDs have been improved dramatically in the past two decades in terms of efficiency and luminance, the stability still remains an issue; the lifetimes of the reported QLEDs are on the order of 100 – 1000 hours with an initial luminance of 100 cd/m², which are far below the requirement for display and lighting applications⁴⁴. Organic materials, such as PEDOT:PSS^{26, 36}, PVK^{26, 41, 42, 71}, poly-TPD^{39, 41, 164} and TFB⁴³ are acting as hole injection\transport layers and Alq₃²⁷ and TPBi^{69, 80} have been used as electron transport layers; however, these organic layers always result in the device degradation when exposed to moisture and air. On the other hand, we notice that there are increasing publications regarding the use of perovskite nanocrystals in replacement of conventional quantum dots as the emitters in the similar planar thin-film LED structures, showing broader wavelength tenability and superior colour purity with narrowband emission (less than 20 nm)²⁰⁰⁻²⁰³. We have already done some preliminary works, demonstrating the strong photo-luminescent

properties and wavelength tunability of perovskite nanocrystals; the corresponded devices need to be fabricated and optimized for further characterization. The detailed plans of my future work are listed below.

7.2.1 Further optimization for all-solution, all-inorganic quantum dot-based LEDs

Due to their superior device stability compared with the organic counterparts, inorganic optoelectronic devices, such as QLEDs and solar cells, are receiving more and more attentions^{105, 131, 141}. However, the performance of current inorganic QLEDs are still not comparable to the best-efficient organic-inorganic QLEDs. It could be partially attributed to the unbalanced charge injection resulted from the different energy barrier holes and electrons encountered or the electroluminescent quenching of QDs from the adjacent inorganic charge transport layers^{184, 204}.

In our previous chapter, we have demonstrated a green-emitting inorganic QLED with a maximum EQE of 1.74% and a brightness over 7,000 cd/m², the highest reported values up to date. In that work, we use solution-processed metal oxide films as the charge injection/transport layers and highlight the use of LiF as an insulating layer to inhibit the quenching effects. The use of LiF on electron transporting side is to optimize the charge balance from both transport layers and diminish the quenching effect from the metal oxide films. The results prove that our scheme can be of significant importance to the improvement of inorganic material-based QLEDs.

Meanwhile, in chapter 5, we have demonstrated a commercially available material - CuSCN as an efficient hole injection material as a replacement for PEDOT:PSS. With its high transparency in the visible range, p-type conductivity, suitable energy band distribution and easy solution processability, CuSCN has proved itself as a qualified candidate as a replacement for the organic

PEDOT:PSS, giving superior or at least comparable performance with the organic counterpart device. Therefore, based on our previous results regarding the replacement of organic charge transport layers and the demonstration of high-performance all-inorganic QLEDs, a further improvement in the choice of charge injection/transport layers and optimized device configuration shall be proposed in this part.

In this proposed inorganic QLED structure, two metal compounds, CuSCN and zinc oxide are applied as the hole and electron injection layers, respectively. Figure 7-1 demonstrates the device configuration with a multilayer structure of ITO/CuSCN/QDs/ZnO/Al in order. As we already demonstrated, CuSCN can be directly spin-coated from its solution; on the other hand, zinc oxide can be synthesized by following the reported sol-gel method with modifications^{41, 205}. In short, high-quality ZnO nanoparticles were acquired by mixing TMAH (in ethanol, 0.55 M) with zinc acetate (in DMSO, 0.1 M) and stirring for 24 h. After that, ethyl acetate was used to participate the nanoparticles and ethanolamine (MEA) and ethanol were applied to dissolve the ZnO nanoparticles for further use. Figure 7-2 shows the transmission electron microscopy (TEM) images of the colloidal nanoparticles with high monodispersity and uniform size (with scale bars = 50 nm and 5 nm, respectively). ZnO nanocrystals are widely applied as the superior electron transport material for efficient charge transportation due to its high carrier mobility and solution processability^{36, 41}.

Figure 7-3(a) shows the flat-band energy level diagram of our proposed inorganic QLED. Holes are injected into the QD layer from ITO and CuSCN while electrons are transported by ZnO from Al cathode. However, since the charge transport materials are both inorganic, quenching effect has to be taken into consideration, as we already demonstrated in previous chapter^{105, 131}. Therefore, similar to what we have done in Chapter 6, buffering/insulating layers might be necessary in order to reduce the quenching effects and further optimize the charge

injection from both sides for better charge balance, as displayed in Figure 7-3(b). It should be mentioned that the choice of such inorganic buffering materials is among the difficulties of this work.

Figure 7-1. Schematic of layers in the device structure.

Figure 7-2. TEM images (a, scale bar = 50 nm) and HRTEM (b, scale bar = 5 nm) of the ZnO nanocrystals dissolved in ethanol.

Figure 7-3. Energy level diagram of (a) the ITO/CuSCN/QDs/ZnO/Al device and (b) ITO/CuSCN/buffering or insulating layer/QDs/ buffering or insulating layer/ZnO/Al device.

7.2.2 An alternative choice: Inorganic CsPbBr_3 perovskite nanocrystals as light-emitting material for solution-processed light-emitting diodes

It takes almost 20 years for quantum-dot based light emitting devices (QLEDs) to be almost comparable with organic counterparts to some degree. However, a latecomer rapidly draws our attentions since the year of 2013, named “perovskite” semiconductor. Due to its high absorption coefficient, high carrier mobility, low defect and low-temperature processability, hybrid organic-inorganic perovskite materials circumvent the problems such the non-radiative recombination due to the high surface defects in QDs and the vacuum sublimation-related high fabrication cost in OLEDs^{200, 206-210}. It has been recognized that a material which is excellent for solar cell material should also be a good candidate for light emission application. Since the power conversion efficiency (PCE) of perovskite solar cells has reached 22.1%²¹¹, the peak EQE of perovskite LEDs also achieve a value of 8.53% with a current efficiency over 42.0 cd/A, which make this type of LED a non-negligible rival to OLEDs and QLEDs, as shown in Figure 7-4 (a)&(b)^{200, 212}.

Perovskite materials normally possess a chemical formula of ABX_3 (A = a monovalent cation, B = divalent metal cation, X = the halide anion), as shown in Figure 7-5²⁰⁶. Currently, the perovskite LEDs with high efficiency use organometallic halide perovskites such as $CH_3NH_3PbX_3$ (methylammonium lead trihalide, MAPbX₃) or $NH_2CH=NH_2PbX_3$ (formamidinium lead halide, FAPbX₃) as emitters^{200, 203, 213, 214}. However, the development of such devices using hybrid organic-inorganic perovskite semiconductors is limited due to the film instability and other related issues^{215, 216}.

Figure 7-4. Development of perovskite LEDs compared with OLED and QLED in (a) EQE and (b) brightness.²¹²

Figure 7-5. The general crystal structure of perovskites (organic & inorganic) with a formula of ABX_3 . The blue, yellow and purple spheres represent the A, B and X atoms, respectively.²¹⁷

On the other hand, inorganic perovskite semiconductor materials, such as $CsPbX_3$ ($X = Cl, Br, \text{ or } I$), occupy superior characteristics over its hybrid counterparts in longer PL lifetime (≈ 2.5 us), smaller exciton binding energy (≈ 35 meV) and better thermal stability²¹⁸⁻²²⁰, which enables it to be an alternative candidate for perovskite-based optoelectronic applications such as photovoltaics, LEDs, lasing and photodetectors^{200, 206, 212, 213, 218, 221-223}. Moreover, the inorganic perovskite nanoparticles possess unique characteristics such as size-relevant tunable bandgaps, narrow emission bandwidths and superior stability, make itself suitable as the emissive material for LED applications²²⁰.

Experimental section:

Materials: Cesium carbonate (Cs_2CO_3 , 99.995%), 1-octadecene (1-ODE, technical grade 90%), oleic acid (OA, technical grade 90%), oleylamine (OLA, technical grade >98%) were purchased from Sigma-Aldrich. $PbBr_2$ (99.999%) was purchased from Alfa Aesar. All materials and chemicals were used as received without further purification.

Preparation of cesium oleate ($Cs(OA)_2$): 0.814 g of Cs_2CO_3 and 40 ml of 1-ODE were mixed into a 4-neck flask and heated for 30 min at 120 °C under degassing, and then 3.1 mL of OA was rapidly injected and further heated to 150 °C under N_2 atmosphere until the solution was transparent. It should be noted that under room temperature, $Cs(OA)_2$ would precipitate in the 1-ODE solution, showing milky white suspensions; therefore the solution should be preheated at 120 °C before injection.

Synthesis of $CsPbBr_3$ nanoparticles: 0.138 g of $PbBr_2$ (0.376 mmol) with 7.5 mL of 1-ODE was loaded into a customized 50 mL four-neck flask, degassing for 10-20 minutes in order to reach a pressure lower than 0.018 mbar under 120 °C.

Then, 1.0 mL of OA was rapidly injected into the mixture during the degassing process; after 1-2 minutes, 1.0 mL of OLA were sequentially injected under argon atmosphere. The cloudy mixture would turn into transparent shortly within three minutes, following by increasing the temperature to 180 °C rapidly. Reports said that the reaction mainly took place within the first 1-3 seconds (based on the characterization of in situ CCD camera-assisted PL measurements²⁰⁷); therefore 0.8 mL of Cs(OA)₂ was swiftly injected and the reaction was kept for 5 seconds. Acetone and ethanol were used to inhibit the further nucleation of perovskite nanoparticles by cooling down the system to room temperature (RT) in short time period. The resultant solution was bright green, as shown in the inset of Figure 7-6.

Purification of CsPbBr₃ nanoparticles: For the first purification process of the crude solution, the centrifugation speed is 10,000 rpm with a duration time of 3 min. Then the supernatants were discarded and 0.6 mL of hexane was added to dissolve the nanoparticles. After the second centrifugation with the same speed and duration, it should be noticed that the supernatant was kept instead of the precipitant. 0.6 mL of hexane, 50 µL of OA, 50 µL of OLA and 1.2 mL of acetone were sequentially added with a following centrifugation of 10,000 rpm with 3 min. After discarding the supernatant, 0.6 mL of hexane was added to dissolve the precipitated nanoparticles for further use.

Characterization of CsPbBr₃ solutions:

It has been reported that CsPbX₃ are more ionic than the chalcogenide-based QDs (CdSe/ZnS and CdSe/CdS QDs), performing a more active interaction with the capping ligands (-OA, -OLA, etc). Therefore the optical properties of CsPbX₃ solutions are strongly dependent on the polarity of the solvents, since some of the polar solvents may cause the photoluminescent degradation or even structure incompleteness by losing the surface ligands of CsPbX₃ nanoparticles²⁰⁸. Researchers noticed that during the isolation and purification cycles, ligands can

be easily “washed away” due to the dynamic binding property, resulting in the decreased photoluminescence intensity and efficiency.

There is a straightforward way to solve the problem: the lost ligands can be compensated by adding the corresponding solvents. For example, appropriate amounts of oleic acid and oleylamine can be added to the intrinsic CsPbX₃ solutions before precipitation to provide the extra but necessary ligands for stabilizing QDs. What’s more, the quantum yield can be further enhanced by adding a small amount of amine (OLA) due to a strongly binding of OA ligand to the surface of nanocrystals²⁰⁷.

The PL quantum yield of the CsPbBr₃ solutions is measured to reach 90% by the absolute PLQY measurement based on the integrating sphere. The PL and UV-Vis spectrum of the resulted CsPbBr₃ solutions are shown in Figure 7-6, giving a first excitonic absorption peak at 500 nm and a Gaussian-shaped PL spectrum with centred wavelength at 514 nm and a FWHM of 19 nm. After spin-coating the solutions onto quartz substrate (20 mg/ml, 800 rpm for 1 minute), the QY of the thin film reaches 50%, which is supposed to be a very high value for applications in light-emitting devices.

Figure 7-6. Normalized PL and absorption spectrum of purified CsPbBr₃ solutions (in hexane), respectively. Inset: the raw CsPbBr₃ solution after cooling down, showing bright green color.

Recent studies have demonstrated that the amount of ligands plays an important role in the film deposition; to be specific, because of the fact that ligands are insulated, excess ligands binding to the nanocrystals will result in the poor charge injection and transportation; on the other hand, insufficient ligands cause the poor structural integrity and low quantum yield²²⁴. Therefore, a trade-off should be always considered in terms of the purification cycles and/or ligand selections. In our case, because excess OA was added in order to preserve the structural stability as well as the PL QY, the electrical properties of the spin-coated films were deteriorated, leading to the device failure.

Researchers have proposed several solutions to solve the ligand-related issues in terms of the interface engineering^{203, 225}, ligand density control²²⁴ and ligand exchange²²⁰. J. Pan et al. demonstrated that by substituting the oleylamine ligand with the halide-ion-pair ligand, CsPbBr₃ device with better charge balance and

improved performance (EQE, CE, etc.) can be achieved²²⁰. Recently, J. Li et al. demonstrated a more suitable way to improve the electrical property of CsPbBr₃ films as well as the final device performance by controlling the ligand density. Such ligand manipulation were realized by choosing a mixture of hexane/ethyl acetate as precipitate to control the ligand density²²⁴. Therefore, our future work will focus on the ligand modulation to find a balance between preserving the high quantum yield and maintaining moderate electrical property in order to fabricate inorganic perovskite quantum dot-based LED with high efficiency, high luminance and better stability.

List of Publications

Journal Paper

1. **Ding, T.**; Yang, X. Y.; Bai, L. Y.; Zhao, Y. B.; Fong, K. E.; Wang, N.; Demir, H. V.; Sun, X. W. Colloidal quantum-dot LEDs with a solution-processed copper oxide (CuO) hole injection layer, **Organic Electronics** 2015, 26, 245.
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3. **Ding, T.**; Wang, N.; Wang, C.; Wu, X. H.; Liu, W. B.; Zhang, Q. C.; Fan, W. J.; Sun, X. W. Solution-processed inorganic copper (i) thiocyanate as a hole injection layer for high-performance quantum dot-based light-emitting diodes, **RSC Advances** 2017, 7, 26322.
4. Wang, N.; Zhao, K.; **Ding, T.**; Liu, W.; Ahmed, A. S.; Wang, Z.; Tian, M.; Sun, X. W.; Zhang, Q. C. Improving Interfacial Charge Recombination in Planar Heterojunction Perovskite Photovoltaics with Small Molecule as Electron Transport Layer, **Advanced Energy Materials** 2017 (DOI: 10.1002/aenm.201700522).
5. Wang, N.; Zhou, Y.; Ju, M. G.; Garces, H. F.; **Ding, T.**; Pang, S.; Zeng, X. C.; Padture, N. P.; Sun, X. W. Heterojunction-Depleted Lead-Free Perovskite Solar Cells with Coarse-Grained B- γ -CsSnI₃ Thin Films, **Advanced Energy Materials** 2016, 6, 1601130.
6. Bai, L.; Yang, X.; Ang, C. Y.; Nguyen, K. T.; **Ding, T.**; Bose, P.; Gao, Q.; Mandal, A. K.; Sun, X. W.; Demir, H. V. A quinoxaline based N-heteroacene interfacial layer for efficient hole-injection in quantum dot light-emitting diodes, **Nanoscale** 2015, 7, 11531.

Conference

1. **Ding, T.**; Yang, X.; Tan, S. T.; Demir, H. V.; Sun, X. W. High Performance Quantum-dot Light-Emitting Diodes Based on Solution-processed Copper Oxide Film. Oral presentation, **ICMAT**, 28 June to 03 July, 2015 Singapore.
2. **Ding, T.**; Wang, N.; Sun, X. W. Solution-Processed Inorganic Copper Thiocyanate Hole

Injection Layer for High-Performance Quantum Dot-based Light-Emitting Diodes. **MRS Fall Meeting & Exhibit**, 27 November to 02 December, 2016 Boston, United States.

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