Colloidal quantum dot light-emitting diode architectures for high performance

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**Colloidal Quantum Dot Light-Emitting Diode
Architectures for High Performance**

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Abstract

Recently scientific research and development on colloidal quantum dot light-emitting diodes (QD-LEDs) have attracted considerable interest thanks to their advantages over conventional epitaxial-based light-emitting diodes, which require expensive deposition tools and high temperature growth on a substrate template, limiting the choices of materials for epitaxial growth. Colloidal quantum dots (QDs) are chemically synthesized tiny nanocrystals that can be easily dispersed in organic/aqueous solvents and integrated into organic/polymer light-emitting diode architectures using cost-effective solution-based fabrication techniques. In addition, the emission spectra of QD-LEDs can be conveniently adjusted (e.g., tuned from blue to red) by simply changing the size of their QDs. This shows a huge potential for future display and lighting applications. Therefore, there is a strong motivation for understanding the underlying device physics and improving the device performance of the QD-LEDs.

This thesis work systematically studies the influence of device architecture on the performance of QD-LEDs using various means including optimizing device charge injection and balance and using efficient indium-free electrodes. In this thesis, white QD-LEDs were demonstrated using a specially designed loosely-packed QD layer and device architecture. In the device, 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) electron transport layer (ETL) and poly(N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)-

benzidine) (poly-TPD) hole transport layer (HTL) were made partially in contact to each other. As a result, a certain amount of the injected electrons and holes recombined at the interface, giving rise to red exciplex emission. Combining the red exciplex emission, the green emission from the QDs, and the blue emission from poly-TPD layer, a set of white QD-LEDs with high colour rendering index (CRI) of 89 and correlated color temperature (CCT) of 4098 K were successfully demonstrated.

Second, an additional HTL was employed between the QD layer and the TPBi ETL to improve the device performance. Adding HTL at the electron side limits excess electrons to be injected into the QD layer, resulting in better charge balance. Here an improvement in the device performance of over five-folds was obtained with the proposed device architecture in comparison to the reference device in which the QD layer is deposited between the HTL and the ETL. The significant improvement results from the balanced hole and electron injection into the QDs emissive layer. Exciton distribution analysis of the studied device showed that nonradiative energy transfer from the organic transport layer to the QDs is minimum and the improvement mainly stems from the optimized charge balance.

Third, the effects of different electron injection materials on the operating voltage were investigated. Notable performance improvement was observed from the devices using Cs_2CO_3 electron injection material. A 35% increase in the EQE, a 19% reduction in the operating voltage, and a 24% improvement in

the power conversion efficiency were achieved compared with the reference device using LiF as the electron injection layer (EIL). Device exciton distribution study showed that Cs₂CO₃ promoted exciton formation in the QD layer and reduced exciton leakage to the organic layer. The increase of exciton recombination in the QD layer thus enabled better device performance.

In addition, in the thesis, we used gallium-doped zinc oxide (GZO) to replace tin-doped indium oxide (ITO) used as the electrode in QD-LEDs due to the increasingly expensive raw materials of ITO. The lowest sheet resistance and resistivity of the radio-frequency (RF) sputtered GZO films are 12.28 $\Omega/\square$ and $9.48 \times 10^{-4} \Omega \cdot \text{cm}$, respectively, comparable to those of commercial grade ITO. These resulting QD-LEDs using the GZO electrodes exhibit a similar level of performance as the devices with ITO as the electrode, indicating that the GZO electrode prepared by the RF sputtering process can be a promising ITO replacement for low-cost QD-LEDs.

QD-LEDs have made great progress in terms of device performance over the years and there is room for further improvement. With all these findings and demonstrations in this thesis, we conclude that QD-LEDs hold great promise for potential applications in lighting and displays.

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List of Abbreviations

AFM	Atomic force microscopy
ALD	Atomic layer deposition
AlGaInP	Aluminium gallium indium phosphide
A.U.	Arbitrary unit
CBP	4'-bis(carbazol-9-yl)-biphenyl
CCFL	Cold cathode fluorescent lamp
CdO	Cadmium oxide
Cd(OA) ₂	Cadmium oleate
CdSe	Cadmium selenide
CdS	Cadmium sulphide
CdS- n -ZnS	Cadmium sulphide core with n layer of zinc sulphide, n is integer number
CdTe	Cadmium telluride
CIE	Commission Internationale de l'Eclairage
CPS	Counts per second
CRI	Colour rendering index
Cs ₂ CO ₃	Caesium carbonate
CTL	Charge transport layer
DI-Water	Deionized water
DMSO	Dimethyl sulfoxide
EIL	Electron injection layer
EL	Electroluminescence
ETL	Electron transport layer
EQE	External quantum efficiency
FRET	Förster resonance energy transfer
FWHM	Full width at half maximum
GaN	Gallium nitride
GaAs	Gallium Arsenide
GZO	Gallium-doped zinc oxide
HDA	Hexadecylamine
HDTV	High-definition television
HIL	Hole injection layer
HOMO	Highest occupied molecular orbital
HTL	Hole transport layer
InAs	Indium Arsenide
InGaN	Indium gallium nitride
InN	Indium nitride
IQE	Internal quantum efficiency
ITO	Indium tin oxide
kWh	Kilowatts-hour
LCD	Liquid crystal display
LED	Light emitting diodes

LiF	Lithium fluoride
LUMO	Lowest unoccupied molecular orbital
MOCVD	Metal-organic chemical vapour deposition
NC	Nanocrystal
NPB	N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'diamine
NTSC	National Television System Committee
OA	Oleic acid
OD	Optical density (Absorbance)
ODA	Octadecylamine
ODE	1-octadecene
OLA	Oleylamine
OLED	Organic light-emitting diode
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
PID	Proportional-integral-derivative
PL	Photoluminescence
PMMA	Poly(methyl methacrylate)
PPV	p-paraphenylene
p-TPD	Poly(N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)-benzidine)
PVD	Physical vapour deposition
PVK	Poly(9-vinylcarbazole)
QD	Quantum dot
QD-LEDs	Quantum dots light-emitting diodes
QY	Quantum yield
rpm	Revolutions per minute
R-SH	Thiols, an organosulphur compound
SSL	Solid-state lighting
TCO	Transparent conducting oxide
TC-SILAR	Thermal cycling coupled successive ionic layer adsorption and reaction
TCTA	4,4',4''-tris-(carbazol-9-yl)triphenylamine
TEM	Transmission electron microscopy
TFB	Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-secbutylphenyl))diphenylamine)]
TGA	Thioglycolic acid
TMAH	Tetramethylammonium hydroxide
TOP	Tri-n-octylphosphine
TOPO	Trioctylphosphine oxide
TOP:Se	Tri-n-octylphosphine selenide
TPBi	(1,3,5-tris(N-phenylbenzimidazol-2,yl)benzene
TPD	N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1-1'-biphenyl-4,4'diamine
UV-Vis	Ultraviolet-visible
YAG	Yttrium aluminium garnet
ZnO	Zinc oxide
ZnS	Zinc sulphide

CHAPTER 1: Introduction

1.1 Thesis Summary

As the fossil fuel resources required for energy generation are increasingly becoming scarce, the near future shortage of fuel has triggered aggressive exploration of alternative energy. However, Singapore is a tiny country, which has limited natural resources and negligible sources of renewable energy including wind, geothermal and hydropower compared to other countries. Hence, boosting energy efficiency thereby reducing energy wastage is the main strategy and one of the focus areas in Singapore [1]. Singapore is targeting to have a 35% improvement in energy efficiency compared to the 2005 levels by year 2030 [1].

Office and residential lightings are main consumers of energy. Therefore, having highly efficient and low power consumption while maintaining certain brightness (typically in the range of $10^3 - 10^4$ cd/m²) lighting is necessary. Light-emitting diode (LED) is one of the promising solutions. The power conversion efficiency of LED is high and able to convert most of the electrical power into light. Fundamentally, this requires three processes to occur: (a) efficient charge injection into the emissive layer (active layer), (b) near unity radiative recombination at the active layer, and (c) efficient light extraction. Additionally, in order to reduce the fabrication cost so that their market retail price is comparable to other light source (e.g.

incandescent lamp and compact cold-cathode fluorescent lamp (CCFL)), the manufacturing process must be simplified and avoid the needs of expensive equipment, such as high vacuum and high temperature systems. Furthermore, use of precious and noble materials should be minimized or replaced by other earth abundant materials.

Colloidal quantum dot light-emitting diodes (QD-LEDs) are potential candidates for the next generation lighting and displays. Colloidal quantum dots (QDs) range in size from 2-20 nm, changing their electronic structures and optical properties in accordance with their size, chemical composition and structure. These nanocrystals are synthesized chemically and capped by ligands and therefore they are dispersible in many aqueous and organic solvents. This allows them to be easily integrated into many organic LEDs (OLEDs) devices by using common low-cost techniques, for examples, spin-coating [2, 3], dip-coating [4], layer-by-layer assembly [5, 6], inkjet printing [7], contact printing [8], and mist deposition [9]. The hybrid combination of inorganic semiconductor nanocrystals and organic semiconductors could allow for a new way to control the exciton formation inside the device and obtain desired emission spectrum. Therefore, better device's luminous efficacy can be achieved as compared to typical white light LEDs that employ broadband emission phosphors.

This chapter provides history and development of various lighting solutions, including incandescent lamp, compact cold cathode fluorescent lamp

(CCFL), and LEDs, followed by the literature study of the QD-LEDs and their advantages, and lead to the motivation of this QD-LEDs study. Challenge of the QD-LEDs and outline of the thesis are given in the last part of this chapter.

1.2 Background

Since the first discovery of fire, and the subsequent inventions of candle light, electric-driven incandescent lamp and CCFL, different types of artificial lighting have become an indispensable privilege in human life. Artificial lighting enables us to extend our live and work during non-sunlit hours, and in turn resulting in a significant improvement in our productivity and life quality. According to the U.S. Energy Information Administration (EIA), the worldwide total power consumption in year 2010 was about 1.53×10^{14} kilowatts-hour (kWh), and it is projected to reach 2.40×10^{14} kWh in year 2040 [10]. Among the total power consumption, about 20% were used for lighting purpose [11, 12]. In addition, it is important to note that artificial light demand in the world is growing at an average of 2.4% per annum and it is expected to increase continuously for the foreseeable future [3, 4] when global population keeps rising and human living standard keeps improving. The dramatic increase in energy supply requirements facing humanity in the 21st century, combined with the negative environmental impacts of fossil fuel combustion and shortage of fossil fuel in near future have led to an urgent need for the large-scale

deployment of renewable energy and energy efficient technologies. This thesis will focus on the energy efficiency on lighting technology.

1.2.1 Incandescent Light Bulb

Incandescent light bulb was commercialized by Thomas Edison. The working principle of incandescent light bulb is thermionic emission in which its element is heated to high temperature until it glows in the visible as a black body. For incandescent light bulb, voltage is applied across two ends of the metal tungsten wire and the resulting electric current flows through the wire. Heat is generated and built up on the tungsten wire owing to the internal resistance of the wire, and when it reaches certain temperature, visible light start to be emitted. Since it is a black body radiation, under same correlated color temperature (CCT, the color temperature of the Plankian black body whose color is closest to the given white light source.), incandescent light has emission spectrum very close to the sunlight and therefore it has excellent color rendering capability. However, thermionic emission involves heating process, most of the input electrical energy ($>90\%$) is loss in the form of heat and invisible infrared light, whereas only a small portion of emission falls in the visible range (400 – 700 nm), resulting in the comparatively low luminous efficiency (<20 lumens per Watt, lm/W) of incandescent light. In addition, metal filament vaporizes over time due to the high operating temperature, leading to unavoidable degradation of light bulb. Therefore, incandescent light bulbs have a relatively short lifetime. Figure 1-1 shows a typical emission

spectrum of the incandescent light bulb at a correlated color temperature of the light is 2856 K calculated using Plank's Law of blackbody radiation equation [13], along with the photopic luminosity function of human eye established by Commission Internationale de l'Éclairage (CIE) [14]. The photopic luminosity function of human eye indicates that human eye is more sensitive to the green wavelength (peaking at 555 nm) and less sensitive to the emission wavelengths below 450 nm and above 650 nm. From the figure it can be found that most of the incandescent light emission cannot be detected by the human eye.

Figure 1-1: (left) Spectrum of a black body radiation at a correlated colour temperature of 2856 K and the human photopic eye sensitivity curve [13, 14]. (right) Typical incandescent light bulb (image adapted from <http://www.usa.philips.com>).

Since the successful commercialization in 1879, there has been no significant breakthrough on the incandescent light bulbs for improving its luminous efficiency. This light bulb is not energy efficient and has short

lifetime, therefore, it is not sustainable. However, in the United States, 90% of the residential sector is still lit up by incandescent bulbs, due to their high color rendition and safety concerns over the cold cathode fluorescent tubes, which will be discussed in the following section. Nevertheless, in order to achieve sustainable development, many countries have initiated the process to phase-out incandescent light bulbs by replacing with more energy-efficient light sources [15-17].

1.2.2 Compact Cold Cathode Fluorescent Lamp (CCFL)

Fluorescence phenomenon was discovered about the same period as the incandescent lamp; however, the commercialization on CCFL took much longer than the incandescent lamps, until solving all the key manufacturing issues.

Figure 1-2: (left) Emission spectrum of a compact fluorescent light tube. (right) Fluorescent light bulb (image courtesy of <http://www.usa.philips.com>).

The working principle of CCFL involves high voltage discharge process in near vacuum environment. Typical fluorescent light tube contains small amount of inert gas, such as argon, krypton, neon, etc. and a little amount of mercury vapour. The pressure inside the light tube is maintained at low level so that discharge process could take place. The tube inner wall is coated uniformly with inorganic fluorescent phosphors, which down-convert high energy photons into visible light. During operation, high voltage is applied across electrodes and the strong electric field can ionize the inert gas nearby. These ionized gas atoms are accelerated by the electric field between two electrodes and move toward the other end. During transportation, they hit other inert gas atoms, or bombard mercury atoms and excite one of the mercury's valence band electrons to higher state. When this energetic electron relaxes and returns back to the ground state, ultraviolet light emits and then is down-converted to visible light by inorganic phosphors.

Compact CCFL can convert electricity into useful light much more effective than incandescent lamps do. To date, the luminous efficacy of a CCFL exceeds 100 lm/W, and achieves up to 24% power conversion efficiency, making it widely adapted and installed in office premises [18]. However, the existence of hazardous mercury vapor may pose a long term environmental issue. In order to have sustainable development, the pursuits of a more efficient and greener lighting solution remain.

1.2.3 Solid State Lighting

During the past 40 years, solid state lighting (SSL) has been being developed rapidly and been widely used in many applications. SSL device, typically referred as light-emitting diode (LED), is an emerging technology with huge potential to exceed the current energy efficiency of incandescent lamps and CCFLs [19]. The working principle behind SSL involves an electroluminescence process, which results from band-to-band radiative recombination of the injected electron-hole pair inside a semiconductor p-n junction. Since the electroluminescence process does not involve heat, light generated by this method can be very efficient, i.e., near unity internal quantum efficiency (IQE) is achievable at the active region. The theoretical power conversion efficiency of LEDs can exceed 300 lm/W, with a proper light extraction technique applied to the device. It is predicted that a 50% reduction of the total energy consumption can be realized if all the current lighting is converted to SSL [20-22]. However, there are still many challenges for the LED technology that have yet to be overcome. Here we classify the light-emitting diodes into three types based on the materials used in the system: inorganic, organic and hybrid organic/inorganic LEDs.

Inorganic LEDs

The first electroluminescence phenomenon was observed by Henry Joseph Round in 1907 when he applied high voltage through a silicon carbide

(SiC) crystal [13]. Since then, electroluminescence has been studied intensively on many direct bandgap semiconductors, leading to demonstration of highly efficient red-emitting inorganic LEDs in early 1962 using a gallium arsenide phosphide (GaAsP) compound semiconductor [23]. Although the external quantum efficiency (EQE) of device is only 0.2%, a lot of studies on the device structures, materials and fabrication methods have been made and now the EQE of LEDs can be as high as 50% [13, 24].

Today, inorganic LEDs are dominated by two material systems that together cover the entire visible window: indium gallium nitride-based (InGaN) system material emitting in the blue/green region and aluminum gallium indium phosphide-based (AlGaInP) material system from yellow to red [25], as shown in Figure 1-4. The power conversion efficiency also improves tremendously and gives birth to the high-brightness LEDs, which are expected to be deployed in next-generation lighting system. In 2013, Cree Inc. announced a high power white light LED with a record breaking power conversion efficiency of 276 lm/W at 350 mA [26], surpassing incandescent light bulbs and CCFL tube.

Figure 1-3: (Left) Emission spectrum of an InGaN/GaN light-emitting diodes (right) A typical LED device from our laboratory.

Figure 1-4: Luminous performance of commercial high-brightness LEDs. The dotted line represents the photopic luminosity function. Figure adapted from [11].

LED device is not a good light source for general illumination purpose due to their narrow full-width at half-maximum (FWHM) of emission spectrum. There are several approaches for white light generation from LEDs, for example, using multiple monochrome LED chips or a single short wavelength LED chip integrated with optically down-converting phosphors to generate long wavelength emission. Multiple chip-driven white LEDs combine red, green and blue LEDs together to generate white light [27, 28]. Since individual LED can be fully optimized to their highest efficiency, this approach promises the highest theoretical efficacy for SSL [29]. One of the challenges of using multichip driven white LEDs is, however, to ensure that the optical efficiency is maintained at high level over the entire visible wavelength (400 ~ 700 nm). To date, high-brightness blue and red light-emitting diodes can be achieved by InGaN/GaN-based and AlGaInP-based LEDs, respectively. However, high efficient green/yellow-emitting LEDs have not been demonstrated yet. Therefore, improving LED performance within the green-yellow gap becomes a major focus in SSL research. In addition, precise electronic control circuit is needed to blend the three monochromatic light sources together and maintain white colour points over a long period. This also increases the cost of production. Therefore, this type of LEDs is mainly for display purposes and is commonly less frequent used for general lighting, although today there are white LED light sources combining red and blue LEDs together with green phosphors used for lighting [29].

Figure 1-5: (left) Electroluminescence spectrum of a phosphor-converted white light LEDs and (right) Philips LUXEON A phosphor converted white light LED module (picture adapted from <http://www.philipslumileds.com/products/luxeon-a>).

White LEDs can also be achieved using a short-wavelength (e.g., blue) LED combined with optically down-converted phosphors, where the phosphors convert certain amount of blue LED pump light into long wavelength (e.g., green and red) emission. With proper amount of phosphors one can tune the LED light output to desired emission spectrum. Since only one blue LED chip is utilized, such phosphor-converted LEDs do not require complicated electronic circuit to control the colour mixing, providing a relatively simple and low-cost white-light solution. The most commonly used broadband yellow phosphor is cerium-doped yttrium aluminium garnet ($\text{Ce}^{3+}:\text{YAG}$), which is integrated on a blue InGaN/GaN LEDs and generate bluish cool white light, and the emission spectrum is given in Figure 1-5.

In fact, due to the lack of a red component, the pale white light cannot express the natural colours of objects faithfully under general circumstances, resulting in a poor colour rendering index score (CRI, which is a measure of light source ability to show how “natural” it render object colour). For indoor applications, warm white LEDs (CCT <4000 K) with excellent colour rendition (CRI > 80) are required. High-efficiency narrowband red phosphor is needed to tune the colour temperature. This is very challenging as commercially available red phosphors have either undesired broadband spectrum or lifetime issues [18]. Furthermore, many inorganic phosphors utilize rare-earth elements as the emitting centre. The scarce rare-earth elements may cause supply issues in the future and lead to a major obstacle for the SSL industry [30]. Instead of using an inorganic phosphor, there are other commercially available organic dyes that are perfect for the application of colour conversion. Organic dyes have a near-unity quantum yield. However, the lack of long-term stability produces technical difficulties for them to be integrated into the SSL [13]. Recently, white light LEDs using inorganic semiconductor quantum dots (QDs) have been demonstrated as an alternative luminophore to inorganic phosphors [31, 32], showing that chemically synthesized colloidal QDs can be one of the promising luminophore candidates for white light generation. QD Vision and Nexxus Lighting commercialized white LEDs using QDs as optical down-conversion phosphors, achieving warm white light with CRI up to 90 at a correlated colour temperature of 2700 K [33]. The colour rendition of an incandescent lamp, a conventional white LED and the white LED utilizing QD

luminophores are shown in Figure 1-6. Incandescent lamps and white LEDs using QD luminophores could generate more appealing illumination compared to other light sources.

Although LEDs have many potentials and advantages over the incandescent lamps and CCFLs, their manufacturing cost is still high due to the uses of ultra-high vacuum deposition and high temperature system. To date, the cost of implementing LED lamp (price of LED lamps and the cost of retrofitting d.c. devices into a.c circuits) still several times higher than traditional lighting solutions. This creates a barrier for consumers to adapt to new technologies. Also, LEDs acting as concentrated point sources might not be suitable for general ambient lighting. For general in-house lighting application, a large-area, diffused light source is preferable.

Figure 1-6: Image showing the effects of incandescent lamp, cool white LED, and the commercial QD-LEDs developed by QD Vision and Nexxus Lighting illuminating the same object. Picture adapted from [33]. Copyright 2010 Co-Action Publishing.

Organic LEDs

Organic materials have been considered for practical electroluminescent devices for long time due to the fact that many of them possess high fluorescent quantum efficiency in the visible window of spectrum. Electroluminescence phenomenon from organic molecule was first observed in 1963 by Pope *et al.* through applying a high voltage on single crystal anthracene [34]. However, further development on the organic electroluminescent devices was not successful. One of the major issues leading to the low device performance was from the low conductivity of organic materials. Organic materials are used to be classified as good insulators and widely used in electrical and electronic sector for insulation purposes. This situation changed after the discovery by Heeger, MacDiarmid and Shirakawa showing that one of the organic materials, polyacetylene, becomes conductive when it is reacted with bromine or iodine vapours [35]. This discovery made three of them being granted the 2000 Nobel Prize in chemistry and opened up an intensive research in conductive polymer science [36, 37].

In 1987, Tang *et al.* from Eastman Kodak company made a significant contribution by introducing a double-layered thin-film organic electroluminescent device [38, 39]. Different from previous reports, their device was operated at low voltage and achieved significant improvement on electroluminescent emission efficiency. Therefore, it is widely recognized as the world's first OLED. Since then, the realization of using organic materials for new generations of organic optoelectronic devices became feasible. In 2009,

Reineke *et al.* reported a white organic light-emitting diode with power conversion efficiency up to 90 lm/W, on par with the CCFL power conversion efficiency [40], showing that OLEDs are potentially promising to replace conventional light sources including incandescent bulbs and CCFLs.

Figure 1-7: Commercially available organic light-emitting panel.

Compared with inorganic semiconductor LEDs serving point sources, OLEDs, while very thin (<200 nm), can be fabricated over large areas, making them large surface-emitting and diffusive light sources. OLEDs can also be deposited on soft flexible substrates, offering great flexibility in the product design and deployment [41]. In addition, due to the broad emission of organic materials, OLEDs typically have high color rendering properties that are close to the incandescent light bulbs. However, to date, most of the organic materials have been found to be oxygen and moisture sensitive. As a result, sophisticated

device insulation is needed to prevent degradation, increasing the fabrication cost.

Quantum Dots LEDs

Since the first electrically driven quantum dot light-emitting diodes (QD-LEDs) were reported [4], a lot of efforts have been put into achieving high efficiency QD-LEDs in the past two decades. Colloidal quantum dots (QD) make inorganic semiconductor nanocrystals with a typical size ranging from 2 to 20 nm [42]. Owing to the quantum confinement effect, QDs show unique size-dependent electrical and optical properties. This gives QDs a narrowband emission that can be spectrally tuned by simply changing the particle size and shape. In addition, surface of QDs is normally passivated by ligands, and depend on the properties (hydrophobic/hydrophilic) of the ligand, allow them to be dispersed in common organic/aqueous solvents. This allows them to be easily integrated into the state-of-the-art OLED fabrication technologies, including spin-coating [8, 33, 43-45], dip-coating [4], layer-by-layer assembly [6], and micro contact printing [46, 47]. Compared to the broad OLED emission, the QD emission features higher color purity, which allows them to display more vibrant, vivid colors [48]. In 2013, Sony, in collaboration with QD Vision, announced a LED TV series named Triluminos display, which use blue LEDs and green, and red QDs to generate back-lighting. The color quality of the new LED-TV can achieve 100% color gamut of the National Television System

Committee (NTSC) high-definition television (HDTV) standard. In comparison, previous LCD displays meet only 60-70% of the NTSC HDTV standard [49].

Figure 1-8: (Top-left) CIE chromaticity diagram. The black dots show possible coordinates of the QD emission [33]. (Top-right) Sony Bravia LED TV using Triluminous display technology (picture adapted from [50]). (Bottom-left) Emission spectra of the QD-LED and phosphor-LED showing better light management of QD-LEDs (Bottom-right) Demonstration of LCD-TV using QD-LED backlights. Reprinted with permission from reference [48]. Copyright 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

While white light solutions using QDs as down-conversion luminophors have been successfully demonstrated and some of them were released into the market, a lot of effort is still needed to improve the performance of electrically-

driven QD-LEDs using QDs as the active emitter. Utilizing QDs as the electrically driven emitters can generate desired light directly and the need of multi-component integration of QDs and optical excitation source (e.g., a high-brightness short wavelength emission LED) could be eliminated. Also, as large-area, diffusive, electrically-driven QD-LEDs are possible [43], electrically-driven QD-LEDs had great promise as future lighting and display candidates.

The first electrically-driven QD-LEDs were demonstrated by Colvin *et al.* in 1994 using cadmium selenide (CdSe) quantum dots and a p-type polymer p-paraphenylene vinylene (PPV) sandwiched between two electrodes. The device schematics is shown in Figure 1-9 [4]. Although the external quantum efficiency of device was rather low ($\sim 0.01\%$) and there was an accompanying significant broad electroluminescence (EL) from PPV polymer, these results quickly received great attention. This work successfully showed that colloidal QDs can not only be optically excited, but also integrate into the LED architecture and be electrically driven to emit light. Since then, notable progress has been made by several research groups to steadily improve the device performance. The improvements mainly come from the efforts of introducing sophisticated deposition tools and methods [6, 46], better device architectures [8, 51, 52] and materials [11, 53-57]. Schlamp *et al.* reported QD-LEDs with improved efficiency up to 0.22% and brightness of 600 cd/m^2 using CdSe/CdS core/shell quantum dots [58] in 1997. The improvement arose from the increase of QD's quantum yield. Later, in 2007, Tan *et al.* demonstrated a bright and color-saturated QD-LEDs using core/shell CdS/ZnS quantum dots and achieve

brightness up to 1600 cd/m^2 [54]. Kwon *et al.* used red, green, blue quantum dots to realise white light generation in 2012 [59].

Figure 1-9: Schematic diagram of the first QD-LED structure. The device consists of an organic charge transport layer and QDs as the active layer.

Today, this device structure is still used in many fundamental studies because of the relatively simple fabrication process. However, lack of an electron injection layer poses difficulties on charge balancing at the QD emissive layer, which results in inefficient exciton formation in the QDs. Charges can recombine at the adjacent organic layer and causes unavoidable parasitic polymer EL. Besides, direct contact of QDs to the electrode quenches QD emission, all of these issues resulting in low device performance.

An improved device structure was introduced by Coe *et al.* in which QD monolayer was sandwiched between two charge transport layers (CTLs), as shown on the schematic diagrams in Figure 1-10 [60]. Instead of using a thick QD layer, their approach of using QD monolayer can prevent charge imbalance in the QD layer. Charge imbalance in QD layer causes QD charging and leads

to undesired Auger recombination, where recombination of electron-hole pair does not emit light but transfers the energy to another charge particle and excites it to higher energy level. The high energy particle will relax and then release energy as form of heat. It is commonly found in the early devices [61]. These improved devices showed a record EQE of 0.54% and brightness level of 2000 cd/m² at that time. Later, Anikeeva *et al.* fabricated QD-LEDs with organic small molecules and different size of QDs using micro-contact printing technique, realized device emission across the entire visible spectrum and achieved a maximum EQE of 2.7% for red-orange QD-LEDs [8], as shown in Figure 1-11.

Figure 1-10: Schematic diagram of the improved QD-LED device structure using double organic charge transport layer, injecting holes and electron from two sides.

Figure 1-11: (Top-left) Photograph of the electroluminescent QD-LEDs, (top-right) EQE (bottom-left) and (bottom-right) current density-voltage (J-V) characteristic of the QD-LEDs using double organic charge transport layers. Reprinted with permission from reference [8]. Copyright 2009 American Chemical Society.

Although recent research on organic semiconductors has reported significant improvement, their conductivity is still low as compared to the inorganic semiconductors. This limits the maximum current density of the QD-LEDs and lower the device performance [62]. To address this issue, inorganic materials such as nickel oxide (NiO) [63, 64], tungsten oxide (WO₃) [45, 65], titanium dioxide (TiO₂) [53], and zinc oxide (ZnO) [43, 56, 66] are often deployed as charge transport layers to enhance the charge injection and mobility. The schematic diagram of this device architecture is shown in Figure 1-11.

Figure 1-12: Schematic diagram of the improved QD-LED device structure using organic/inorganic charge transport layer.

For this device architecture, Caruge *et al.* first showed that inorganic NiO film can be an efficient hole transport material to replace the commonly used N-N'-diphenyl-N,N'-bis(3-methylphenyl)-1-1'-biphenyl-4,4'-diamine (TPD) in the devices and obtained a maximum device EQE of 0.18% [63]. Subsequently, they replaced organic electron transport layer with an intrinsic n-type ZnO film and successfully demonstrated all inorganic QD-LEDs, which can be operated at a record breaking current density of 3.5 A cm^{-2} [64], shows that inorganic charge transport layer has advantage over organic charge transport layer at high current level. Qian *et al.* demonstrated QD-LEDs using solution-processed zinc oxide (ZnO) nanoparticles as ETL, while keeping the HTL to be organic polymer (poly-TPD), and achieved blue ($\lambda_{\text{em}} = 470 \text{ nm}$), green ($\lambda_{\text{em}} = 540 \text{ nm}$), and red ($\lambda_{\text{em}} = 600 \text{ nm}$) emitting devices with luminance levels up to 4200, 68000, and 31000 cd m^{-2} and maximum external quantum efficiencies (EQE) up to 0.33, 1.8 and 1.7%, respectively [56]. Kwak *et al.*

reported an inverted device architecture using ZnO nanoparticles as ETL and fabricated blue, green, and red devices with maximum brightness of 2250, 218 000, and 23 040 cd m^{-2} and maximum EQEs of 1.7, 5.8 and 7.3%, respectively [43]. In 2013, QDVision company reported a red emitting QD-LED with near-unity internal quantum efficiency (IQE) and 18% EQE by improving the charge injection of the devices. All of these reports reveal the huge potential of electrically-driven QD-LEDs as a prospective next generation lighting solution [67].

1.3 Challenges of QD-LEDs

Although extensive research in the past two decades has discovered the potential of QD-LEDs, there are several issues to be addressed before they can be deployed at large scale in display and lighting applications. The main challenge of the QD-LEDs is their efficiency. To date, effective procedure to systematically improve the device performance is still lacking. Unlike high-power inorganic LEDs and OLEDs, which have sophisticated and reliable simulation tools to shorten the device research and development duration, the device physics behind QD-LED technology has not been fully understood. This therefore makes exploration of QD-LED technology challenging and time consuming. In addition, compared to other lighting sources, the fabrication cost of QD-LEDs is relative higher. Finding a way to reduce the fabrication cost is also one of the challenges to be addressed.

1.4 Thesis Organization

This thesis systematically studied the influence of device architecture on the performance of QD-LEDs by optimizing device charge balance and using efficient indium-free electrode. The thesis organization is as follows:

Chapter 1 reviews the history and development of different lighting solutions, including incandescent lamps, CCFL lamps, inorganic LEDs, organic LEDs and QD-LEDs, followed by the recent advances of QD-LED development. Besides, key challenges to QD-LED development are discussed.

Chapter 2 covers the basic working principles of the LED technology, size-dependent properties of QD and the mechanisms involved QD-LED operation to provide a better understanding of the underlying physics behind the QD-LEDs.

Chapter 3 details the experimental setup and techniques used in the QD fabrication and characterization. The method of QD synthesis is firstly described, followed by the layer-by-layer deposition of the device films. Characterization methods are also given here.

Chapter 4 discusses an effective method to realize white light emission from QD-LEDs using loosely packed QD films.

Chapter 5 provides a simple yet efficient way to improve the efficiency of QD-LEDs by sandwiching the QD layer inside the hole transport layers and the underlying physics is discussed.

Chapter 6 studies the effects of the electron injection layer to effectively reduce the device operating voltage and resulting in power conversion efficiency improvements.

Chapter 7 addresses the increasingly expensive for the raw materials of the commonly used tin-doped indium oxide (ITO), and discusses the uses a more earth-redundant alternative transparent conductive electrode to fabricate QD-LEDs, to have sustainable development.

Chapter 8 summarizes the thesis work and concludes with proposing several possible future steps.

CHAPTER 2: Literature Review of QD-LEDs

Physics

2.1 Operating Principle of LEDs

Light-emitting diodes (LEDs) are basic electronic components that emit light when they are being electrically driven. LED bond a p-type semiconducting material with another n-type semiconducting material and form p-n junction at the interface of the two layers. Under bias, electric current flow through the LED where holes and electrons meet together at the junction, recombine and emit light. The schematic diagram illustrating the emission process is shown in Figure 2-1.

The energy of the emitted light is characterized by the forbidden band gap between conduction band and valence band, also known as the bandgap E_g of the semiconductor. The semiconductor bandgap energy is the minimum energy required to excite a valence band electron to the conduction band. On the other hand, it also determines the energy of a photon being produced when an excited electron on the conduction band recombines with a hole in the valence band. When electrical current is passed through LED, electrons in the conduction band flow across the junction from the n-doped materials, and holes in the valence band are injected from the anode into the p-doped material. They meet at the junction and recombine, emitting photons with energy equal to the bandgap:

$$E_g = h\nu \quad (2.1)$$

where E_g is the bandgap energy of the semiconductor, h is the Plank's constant, and ν is the frequency of the emitted light.

Figure 2-1: Energy band diagram of light emitting diodes under (top) zero bias and (bottom) forward bias voltage.

This energy transformation usually occurs in the direct bandgap materials (e.g., zinc oxide (ZnO), gallium nitride (GaN)), whereas their highest energy of

the valence band and the lowest energy of the conduction band have the same k wave vector. In this arrangement, electron and hole can recombine directly and emit one photon. In contrast, for an indirect bandgap material its lowest energy of conduction band and the highest valence band energy are not aligned in k -space. Due to the conservation of energy and momentum, recombination of electron and hole will require photon and phonon interaction. Since multiple particles are involved in the transition process, the radiative recombination rate is lower than that of the direct bandgap materials. As a result, direct bandgap materials are commonly used to achieve efficient light emission. The schematic energy band diagrams of the direct bandgap and indirect bandgap materials are shown in Figure 2-2.

Figure 2-2: Schematic band diagram for (left) direct bandgap and (right) indirect band gap semiconductor.

In fact, one can fabricate LEDs using a particular semiconducting material that has the required bandgap and therefore emits the desired colour of light. However, the bandgap is an intrinsic characteristic of each semiconductor material, and in order to achieve all the desired colours, bandgap engineering is necessary. One of the methods for bandgap engineering is performed by mixing two semiconductors in a form of alloys to control or alter the effective bandgap. For example, indium nitride (InN) and gallium nitride (GaN) are mixed and grown in a form of ternary alloy (indium gallium nitride, InGaN), which has an effective bandgap energy lying between the bare GaN and InN bandgap. Different compositions of alloy are employed to tune the bandgap of semiconductor for the desired emission wavelength. Figure 2-3 shows the possible semiconductors on earth which has a direct bandgap ranging from infrared to ultraviolet window and the potential candidates of semiconductor alloys that have a particular optical bandgap for light-emitting applications.

The basic p-n junction LED discussed above suffers from low light-emitting efficiency. As the emitted photon carries same energy to the bandgap of the semiconductor material, the light generated at junction could be absorbed by the material itself and re-excite electron from the valence band to conduction band. This photon reabsorption process is indeed undesirable for LEDs as it will decrease the device internal quantum efficiency, which is defined as the ratio of emitted photons to the injected electron-hole pairs. As a result, this process should be eliminated. This issue was addressed and solved by introducing double heterojunction to the LEDs in late 1960s [26].

Figure 2-3: (left) Bandgap versus chemical bond length of compound semiconductors that have bandgap in the visible spectrum windows. Due to different lattice structure, chemical bond length (interatomic separation) is shown here. (right) Different colour of light generated from binary/ternary/quaternary material systems. Reprinted with permission from Reference [68]. Copyright 1997 Nature Publishing Group.

Double heterojunction is a structure that contains two or more semiconductors with different bandgaps. The smaller bandgap semiconductor is sandwiched by larger bandgap materials, as shown in Figure 2-4. Under voltage bias, carriers are injected and move toward the junction, and lastly being trapped in the smaller bandgap semiconductor. As carriers are confined inside the smaller bandgap semiconductor, the light emission is determined by the smaller bandgap material rather than the larger bandgap material. This device structure has shown increased light-emission efficiency as the wide bandgap material is optically transparent to the emitted photons. Due to the invention of double heterojunction, LEDs with this device architecture had achieved performance surpassing that of the conventional red-filtered incandescent lamp [27]. Further improvement was achieved by reducing the thickness of

sandwiched material to several nanometers, where the light output is affected by quantum confinement effect. The reduced-thickness film, commonly known as quantum well, still appears in the state-of-the-art LEDs.

Figure 2-4: Bandgap diagram of a double heterojunction LED structure under forward bias. During forward bias, electrons from the n-type semiconductor and holes from the p-type semiconductor move toward each other and recombine at the sandwiched smaller bandgap semiconductor and release the energy difference in the form of photons.

2.2 Semiconductor Nanocrystals

2.2.1 Size-dependent Property of Quantum Dot

The research on the semiconductor nanocrystals, also known as colloidal quantum dots (QDs), has been intensively pursued in the past three decades, not just for the fundamental scientific interest, but also for their potential applications in bio-sensing [69, 70] and optoelectronic applications such as light-emitting diodes and solar cells [33, 42, 47, 62, 71]. QDs are typically group II-VI, III-V, I-III-VI semiconductor compounds, are tiny crystalline particles which exhibit unique size-dependent optical, magnetic, electronic, and

chemical properties that cannot be otherwise observed from their bulk compounds. These nanocrystals bridge the gap between the small molecules and the bulk crystals. They have not only discrete electronic transitions as we have seen on isolated atoms and molecules but also some useful properties, which only exist in the crystalline materials. Their size and corresponding energy states are illustrated in Figure 2.5.

Figure 2-5: Electronic energy states of a semiconductor in transition from a single atom into small cluster, quantum dot and a bulk crystals.

The size-dependent properties of the QD arise from the quantum confinement effect, which is observable when the dot's size is reduced down to the level that is comparable or smaller than the Bohr radius a_B . Bohr radius is a dimension that describes the spatial extension of the exciton in the semiconductor. Depending on the semiconductor composition, the Bohr radius could vary from 1 to more than 100 nm and it can be calculated as

$$a_B = \frac{\hbar^2 \varepsilon}{e^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) \quad (2.2)$$

where ε is the dielectric constant of the semiconductor materials, $\hbar$ is the reduced Plank constant, e is the charge of an electron, m_e and m_h are the effective mass of the electron and hole, respectively. When the radius of QDs becomes comparable to a_B , the barrier potential will start confining the exciton's wavefunction, inducing change in the electronic density of states and the separation between the energy levels. This is manifested as an increase in the semiconductor bandgap, or equivalently, the HOMO-LUMO gap (E_g) resulting in the blue shift of the first excitonic peak on the absorption and photoluminescence spectra.

In order to understand the quantum confinement effect and predict how it affects the QD energy level, we start with the “particle-in-a-box” approach which was developed by L.E Brus [72]. This model successfully explains why the gap between the neighbouring energy levels increases with the particle size, and how we tune the bandgap by simply changing the particle size. First, we assume a spherical particle is surrounded by infinite potential barrier in the case of one-dimensional space. The steady-state Schrödinger equation is given by [73]

$$-\frac{\hbar^2}{2m} \frac{d^2 \phi(x)}{dx^2} + U(x) \phi(x) = E \phi(x) \quad (2.3)$$

where $\phi(x)$ is the wave function of the charge particle (either electron or hole), m is the effective mass of the charge particle, E is the energy of the states and $U(x)$ is the potential profile of the box with a width a , which is defined as:

$$U(x) = \begin{cases} 0, & |x| < a/2 \\ \infty, & |x| > a/2 \end{cases} \quad (2.4)$$

The wave function (Equation 2.5) and the energy spectrum of the charge particle at discrete levels E_n (Equation 2.6) are given below [73]:

$$\phi(x) = \begin{cases} \frac{\sqrt{2}}{a} \cos \frac{n\pi}{a} x, & n \text{ is odd} \\ \frac{\sqrt{2}}{a} \sin \frac{n\pi}{a} x, & n \text{ is even} \end{cases} \quad (2.5)$$

$$E_n = \frac{n^2 \hbar^2 k^2}{2m^* a^2} \quad (2.6)$$

where n is an integer number, and the minimum of particle energy in the infinite well is the energy E_1 , also known as the particle zero energy:

$$E_1 = \frac{\hbar^2 k^2}{2m^* a^2} \quad (2.7)$$

It is clear that the energy levels of the particles become discrete and the particle ground state energy is not “zero”, but a value E_1 above the band edge. The solution plot (wavefunction and the energy) of the Schrödinger equation for a charge particle placed inside an infinite rectangular potential well is shown in Figure 2-6.

Figure 2-6: Energy states and corresponding wavefunctions for a one-dimensional potential well with infinite wall [73].

Combining the intrinsic bulk semiconductor bandgap, their carrier kinetic energy and Coulomb interaction, the size-dependent bandgap energy of the semiconductor nanoparticles is given in Equation 2.8 [73]:

$$E_g^* = E_g + \pi^2 \left(\frac{a_B}{a} \right)^2 R_y^* - 1.786 \left(\frac{a_B}{a} \right) R_y^* - 0.248 R_y^* \quad (2.8)$$

where E_g^* is the size-dependent bandgap, E_g is the bulk bandgap of the semiconductor, a_B is the Bohr radius, a is the radius of the semiconductor quantum dots, R_y is the Rydberg unit of energy, which corresponds to the lowest ionization energy to ionize a hydrogen atom from its ground state. It has a mathematical formula given as follows:

$$R_y = \frac{e^2}{2a_B} \quad (2.9)$$

2.2.2 “Top-down” and “Bottom-up” Approaches For Nanocrystal Synthesis

There are many ways to synthesize nano-sized materials, and they can be classified into two main groups: top-down approach and bottom-up approach. Top-down approach creates nanostructures by sub-10 nm lithography combined with etching processes. Due to the light diffraction limit, nanometer-range patterning using conventional optical lithography is not feasible yet expensive. Instead, e-beam lithography [74, 75], X-ray lithography [76-78], direct two-photon beam writing [79], nano-imprint lithography [80], and dip-pen nanolithography [81] have been employed. QDs are made by either directly writing onto the substrate or using photo-sensitive chemicals (photoresists) followed by a standard etching process.

On the other hand, we can grow nanocrystals using bottom-up approach, either using epitaxial or chemical methods. Reported in 1939, Stranski-Krastanov mechanism relies on self-organization which grows quantum dots by manipulating the lattice mismatch between the substrate and the epitaxial film [82]. The growth initially starts by growing epitaxial films layer-by-layer up to several monolayers thick until islands are formed when the thickness of the films exceeds the critical layer thickness. The size of the quantum dots strongly depends on the growth parameters, strain/stress caused by the lattice mismatch between two films and chemical potential of the deposited film. Such quantum dots are often in pyramid shape and the size range from 5 to 20 nm.

Figure 2-7 shows the schematic illustration and the AFM image of the indium arsenide (InAs) epitaxial QDs. It is estimated to have 5×10^{10} dots/cm².

Figure 2-7: (left) Schematic illustration of Stranski-Krastanov growth based quantum dots. When the epitaxial film was few monolayers, no quantum dots were observed. Increasing the number of monolayers to exceed the critical thickness leads to transition from the layer-to-layer growth to island-based growth, and quantum dots occurred. (Right) AFM image of InAs quantum dots on GaAs substrate, showing the large number of quantum dots formation. Reprinted with permission from Reference [82]. Copyright 2004 Annual Reviews.

The QD density is estimated to be more than 10^9 cm^{-2} by using Stranski-Krastanov growth method. However, it is difficult to control the size precisely. This results in broadening of the emission spectrum. Besides, due to the tiny size, the quantum dot surface is rich of defects, which can affect the emission efficiency. Instead of recombining radiatively, electron-hole pairs may recombine via trap states with no light emission. In contrast, colloidal chemistry synthesis can synthesize more uniform nanocrystals with desired sizes and shapes by simply manipulating the reaction condition, which will be discussed in the next section [83].

2.2.3 Reaction Mechanism Behind Colloidal Quantum Dot Synthesis

Colloidal nanocrystals can be synthesized by reacting appropriate amount of precursors in a reaction medium. In the early research, pyrophoric organometallic compounds were commonly used as the reaction precursors, and later, they were replaced by inorganic salts, which are less hazardous and provide better stability [84]. Colloidal nanocrystal synthesis involves four consecutive stages: (a) nucleation stage from the initial homogeneous solution, (b) growth of the nuclei, (c) growth termination by isolation of particles while the nanocrystals reach the desired size, and (d) post-preparation treatments [42].

The mechanism of the QD synthesis was described by the model proposed by La Mer and Dinegar on colloidal particle nucleation and growth [85], as shown in Figure 2-8. Before injection ($t < 0$ s), one of the precursor solutions is carefully maintained at supersaturation stage and ensured that no nuclei is formed during this period. During synthesis ($t > 0$ s), another precursor is injected into the hot coordinating solvent to initiate the nucleation process. Compared to homogeneous nucleation, which requires high activation energy, heterogeneous nucleation could take place at a relatively low temperature. Due to the high temperature, the injected precursor decomposes quickly and the entire precursor concentration increases to exceed the nucleation threshold, leading to the rapid nuclei formation. This formation process will consume a lot of precursors and quickly reduce precursor's concentration level below the nucleation threshold. Immediately the nucleation process stops and moves

toward the growth stage, whereas nuclei grow larger as long as precursor exists in the solution. Since all the particles nucleate at the same time, their size variation is very small at this stage. In many cases, the synthesis will immediately go to the second growth process, which is known as Ostwald ripening. At this stage, small particles will dissolve and diffuse to larger particle. The number of nanoparticles is therefore reduced and their mean size increases. In nanoparticle synthesis, this is undesirable as the size dispersion will increase by 15~20% [86]. Reaction is normally stopped before reaching this stage.

Figure 2-8: (a) Schematics illustrating La Mar's model for the stage of nucleation and growth for the monodispersed colloidal particles. (b) Experimental setup for monodispersed quantum dot nanocrystals synthesis. Reprinted with permission from Reference [87]. Copyright 2000 Annual Reviews.

The optical properties of semiconductor nanocrystals depend on their structure. However, as the crystal size reduces, there will be more atoms on the surface, i.e., the surface-to-volume ratio increases. Atoms on the nanocrystal's surface are not as completely bonded as what they are in the bulk crystal lattice. The crystal periodicity is interrupted and dangling bonds are formed on each surface atom pointing outward from the crystal. These dangling bonds could introduce new energy levels within the HOMO-LUMO gap, forming trap states that lead to strong carrier localization and reduce the overlap of electron and hole wavefunctions. In addition, this creates a nonradiative decay pathway, which has a lifetime much faster than the radiative recombination. In order to minimize the nonradiative recombination, QD surface is either passivated with surfactant molecules (ligands) or overcoated with different semiconductor materials, which shifts the defect-rich surface away from the core and minimizes the dangling bonds.

2.2.4 Surface Passivation of Quantum Dots by Ligands

Nanocrystal surface is rich of defects, which can be nonradiative decay centers during exciton relaxation [42, 88]. Surfactants, also known as ligands, are used to overcoat nanocrystals surface during the synthesis. Ligands can attach to the nanocrystal surface and form ligand-metal bonds, which can reduce the dangling bonds and minimise the defect states. Compared to the bare

semiconductor nanocrystals, nanocrystals coated with ligands could achieve higher luminescence quantum efficiency and better stability [89].

In addition to nanocrystals surface passivation, ligands also play a key role in the synthesis. During synthesis, certain ligands would interact with nanocrystals while there are ligands that could directly interact with the monomers. For example, tri-octylphosphine (TOP) reacts with elemental sulphur to form tri-octylphosphine sulphide (TOP:S), which serves as a sulphur source in the synthesis. By carefully choosing the nucleation and growth temperature, concentrations of the precursors and the passivating ligand, the solvent type and the growth time, we can synthesize nanocrystals with desired size (dots (0D), rods (pseudo-1D), nanowire (1D), tetra-pods (2D), and disks (2D)) and shapes [90].

Typical ligands consist of polar head group at one end. The polar head contains functional groups of phosphine (-P), carboxylic acid (-COOH), thiol (-SH), and halide (-X), which coordinate the metallic or ionic atoms in the solution and on the surface of nanocrystals. On the other hand, the non-polar hydrocarbon determines the interaction between the surfactant layer and surrounding medium. QDs are inorganic materials which are less soluble in organic solvents. However, with the aid of organic ligands, they can form stable suspensions inside the organic solvent without having aggregation or fusion. Their quantum efficiency, chemical stability and electronic properties (e.g.,

conductance) are strongly influenced by the type of ligands attached on it, as summarised in Table 2-1 [42].

Table 2-1: Different types of commonly used surface ligands for nanocrystals. Data adapted from [42].

Ligand type	Molecule with a single head group and a long hydrocarbon chain	Molecule with a single head group and a short hydrocarbon chain	Cross-linking molecules with two head groups	Metal chalcogenide group
Structure
Interparticle spacing	>1.5nm	0.3~1nm	0.3~1nm	>0.5nm
Preparation method	Addition of ligand during synthesis	Addition of ligand during synthesis or ligand exchange	Treatment of nanocrystals with a linker	Ligand exchange
Stability	Stable	Decrease stability compared to long hydrocarbon chain	Decrease stability compare to long hydrocarbon chain	Decrease stability compared to long hydrocarbon chain
Conductivity	$10^{-12} \sim 10^{-9} \text{ S cm}^{-1}$	$10^{-1} \text{ S cm}^{-1}$	$6 \times 10^{-3} \text{ S cm}^{-1}$	$\sim 200 \text{ S cm}^{-1}$

Using ligands to passivate QDs had been proven to improve the nanocrystals stability and enhance the QD's photoluminescence. However, it is technically very difficult for one type of ligand to simultaneously attach onto the QD cationic and anionic surface sites. In addition, ligands will degrade over time and detach from the surface, resulting in weaker passivation of the QD surface. Therefore, there are always some dangling bonds on the nanocrystal's surface, which will unavoidably reduce the quantum yield [91].

2.2.5 Core/Shell Quantum Dots

An important strategy to improve nanocrystal surface passivation is to overcoat nanocrystals with an inorganic shell using different semiconductor materials. Inorganic epitaxial growth on the nanocrystals core can efficiently eliminate both cationic and anionic surface dangling bonds. This core/shell system is normally accompanied by a small red shift in the first excitonic and emission peak, which is due to the leakage of electron and hole wavefunction into the shell that reduces the ground state energy E_1 .

Depend on the energy difference between the conduction band and valence band of the core and shell materials, the electron and hole will encounter different localization regime. Based on the localization of electron and hole wavefunctions, they can be categorized into three types: type-I, type-I^{1/2} (also known as quasi type-II), and type-II. For the type-I nanocrystal, the bandgap of core material lies completely within the shell material, and the wavefunctions of the electron and hole are confined inside the core. Excitons no longer sense the dangling bonds as the core atoms at the interface are now bounded to the shell atoms. Therefore this type of core/shell QDs can achieve superior quantum efficiency and photostability. For light emitting purposes, type-I core/shell QDs is preferable. There are some cases in which one of the carriers is confined in the core volume while the other carrier delocalizes over the nanocrystals, due to the small energy band offset. Such core/shell systems are classified as type-I^{1/2} QDs. Compared to type-I QDs, they have relatively

longer exciton lifetime, which makes them a potential candidate for lasing application.

Figure 2-9: Schematic diagram and the energy band structure of (left) CdSe (core)/ZnS (shell), (middle) CdSe (core)/CdS (shell), and (right) CdSe (core)/CdTe (shell) nanocrystals. The red and blue curves indicate the probability of finding carrier in the system. In this diagram, CdSe/ZnS and CdSe/CdS are type-I, while CdTe/CdSe represent type-II system. Reprinted with permission from Reference [42]. Copyright 2009 American Chemical Society.

Type-II core/shell QDs have spatial indirect exciton, i.e., one of the carriers (a hole or an electron) is confined in the core, while another carrier is confined in the shell layer. Due to the less overlap in the electron and hole wavefunction, the exciton takes longer time to recombine, leads to longer radiative lifetimes and increases exciton polarisability. As the exciton recombination takes place at the QD core/shell interface, they can emit photon with energy lower than the bandgaps of individual materials. This opens up an access to the wavelengths that are not accessible by standalone core. In order to achieve type-II localization regime, the shell layer has to be reasonably thick. Thin shell can only yield type-I^{1/2} nanocrystals. The spatial separation of exciton and long carrier lifetime have generated attention to make single

exciton lasing feasible [92]. However, a relatively low quantum yield compared to type-I nanocrystals and near infrared emission make it not suitable for visible light-emitting applications. The schematic representation of the band structure and the corresponding carrier's wavefunctions of commonly found CdSe core/ZnS shell (type-I), CdSe core/CdS shell (type-I^{1/2}), and CdSe core/CdTe shell (type-II) QDs are shown in Figure 2-9.

Epitaxial shell growth is generally required to obtain core/shell nanocrystals with satisfactory optical properties. For choosing a suitable shell material, the energy band alignment between the core and shell materials is not necessary to be well aligned. Instead, the more important factor is their lattice structure and lattice parameter. Different lattice structure or large mismatch can introduce a local trap state for charge carriers that open up new nonradiative decay pathways and quench the fluorescence quantum efficiency. Therefore, to obtain zero defects at the core/shell interface, the two chosen materials must have sufficiently small lattice mismatch.

2.3 Emission Mechanisms of QD-LEDs

In QD-LEDs, the QD layer can emit light based on the four emission mechanisms: (a) direct optical excitation of the QDs, (b) charge injection into the QDs, (c) nonradiative energy transfer from the wide bandgap materials to the QDs, and (d) emission due to the field-induced QD ionization. These four

mechanisms can occur simultaneously, and we will discuss these mechanisms in the following subsection.

2.3.1 Optical Excitation of QDs

QD emits light when it is being photo-excited, which has energy equal or larger than the effective bandgap of the QD. Detail of the mechanism is shown in Figure 2-10.

Figure 2-10: Emission of QDs due to optical excitation.

For a QD-LED device, this emission mechanism takes place when the injected holes and electrons recombine outside the QD layer (e.g., in the charge transport layer) and emit photons with energy equivalent to the bandgap of the layer. The charge transport layers are carefully chosen to have a bandgap larger than the QDs so that they are optically “transparent” to the photons emitted by

QDs. QDs will be excited and emit light with photon energy equal to the QD's bandgap.

In order to fully utilize this emission mechanism, the QD layer must be thick enough so that they can harvest all the high energy photons and convert them into the QD emission. However, due to the insulating ligands covered on the QD surface, thick QD layer will make the charge injection more difficult and decrease the overall device performance. Therefore, this emission route is seldom deployed in thin-film QD-LEDs but widely found in the down-converted QD-LEDs. For this configuration, a thick QD film is moved out of the device and the excitation source is replaced by a high-brightness blue InGaN/GaN LED [31, 32, 93].

2.3.2 Förster Resonance Energy Transfer (FRET)

Förster resonance energy transfer (FRET) is a dipole-dipole interaction between donor (here we refer to the organic charge transport layer that has larger bandgap) and acceptor (e.g., QDs). In this process, exciton energy of donor is transferred to acceptor nonradiatively and an exciton is created at the acceptor. Details of the FRET mechanism are illustrated in Figure 2-11.

Figure 2-11: Emission of QDs using Förster resonance energy transfer (FRET).

In order to obtain significant FRET process, donor and acceptor must be close enough, and emission spectrum of the organic molecule and QD absorption spectrum should have good spectral overlap as the rate of nonradiative energy transfer is proportional to these two factors. The Förster nonradiative energy transfer rate k_{FRET} between donor and acceptor is given by [94]

$$k_{FRET} = \frac{1}{\tau} \left(\frac{R_0}{r} \right)^6 \quad (2.10)$$

where r is the spatial distance between donor and acceptor, τ is the donor lifetime, and R_0 is the Förster radius, which is calculated using

$$R_0^6 = \frac{9 \ln(10) \kappa^2 \phi_{QD}}{128 \pi^5 n^4 N_A} \int_0^\infty \frac{F_D(\omega) \epsilon_A(\omega)}{\omega^4} d\omega \quad (2.11)$$

here κ^2 is the orientation factor (which has value of 2/3 for randomly oriented dipoles), ϕ_{QD} is the donor fluorescence quantum yield, n is the refractive index of the medium (in our case typically $n = 1.7$), N_A is the Avogadro's number, F_D is the normalized donor emission spectrum, ϵ_A is the acceptor molar extinction coefficient, and ω is the wavenumber of the particular wavelength ($\omega = 1/\lambda$).

Figure 2-12: Illustration of the FRET process. When donor/QD acceptor distance r is larger than Förster radius R_0 , energy transfer between donor and QD acceptor does not occur and donor emission is observed. When $r < R_0$, donor transfer its exciton energy to the QD acceptor, result in donor emission quench and QD acceptor emission is observed.

QD emission via FRET process was reported to be the dominant mechanism in QD-LEDs using double-sided organic charge transport layer with a close-packed monolayer QD film [8, 52]. The hole and electron recombine at the interface between organic charge transport layer and QD layer. If it is within

the Förster radius, exciton energy is able to transfer nonradiatively into QDs and promote QD emission.

2.3.3 Direct Charge Injection

Direct charge injection is the main operating mechanism in many LEDs, in which electron injected from the ETL side and hole from the HTL side recombine in the active layer (here we refer to the QD layer) and emit light. Schematic of the direct charge injection mechanism is shown in Figure 2-13.

Figure 2-13: Emission of QDs using direct charge injection.

In order to have efficient charge injection into the QDs, the energy barriers at every interface should be minimal so that they do not block the charge injection into active layer. However, the energy barrier for minority carrier should also be large enough to minimize carrier leaks from the active layer. More importantly, rate of electron and hole injection should be balanced

so that charges do not accumulate in the QD. Any QD in the charged state will lead to undesired Auger recombination. To date, most of the high efficient QD-LEDs rely on this emission mechanism.

2.3.4 Field-induced QD Ionization

QD excitation due to field-induced ionization was first observed and confirmed in electron-only single carrier devices when large electric field was applied over the device [95]. With high voltage bias, electron can be extracted from the valence band of a QD and tunnel to neighboring QD and become a free electron, leaving behind a hole in QD. This free electron can recombine with hole and lead to radiative recombination. Detail of the mechanism is shown in Figure 2-14.

Figure 2-14: Emission of QDs via field-induced ionization.

CHAPTER 3: Experimental Setup and Methodology

In this chapter, synthesis of colloidal QDs is first discussed, followed by device fabrication using solution process and thermal evaporation methods. Various QD-LED device characterizations will also be elaborated in the last section.

3.1 Colloidal Quantum Dot Synthesis

There are numerous ways to synthesize colloidal QDs. In this thesis we categorize them into two main kinds based on the type of solvents used during the synthesis, (a) aqueous solvents (e.g., water) vs. (b) organic solvents (e.g., trioctylphosphine oxide (TOPO), 1-octadecene (1-ODE)). Experimental setup used for general QD synthesis is described in the first subsection, followed by few featured QD synthesis methods used in the thesis, including cadmium selenide (CdSe) QDs, core/shell structure cadmium selenide/zinc sulphide (CdSe/ZnS) QDs, one-pot alloyed cadmium-zinc-selenide-sulphide (CdZnSeS) QDs with composition gradient in organic solvent. Additionally, details of nanocrystal purification and characterization are discussed in the following subsection.

3.1.1 Experimental Setup

Typical QD synthesis setup is shown in Figure 3-1. The setup consists of a heating mantle equipped with continuous stirring function, a temperature probe connected to a proportional-integral-derivative (PID) type temperature controller to precisely control the reaction temperature (with a tolerance of ± 2 °C), a 3-neck flask where the synthesis will take place, a condenser for refluxing purpose, and a Schlenk line used to switch between argon and vacuum environment, a scroll pump to provide vacuum environment and a purified argon cylinder with 5N (99.9995%) purity. QD is recommended to be synthesized in inert gas (e.g., argon/ nitrogen) environment because some precursors (trioctylphosphine (TOP), selenium) are very sensitive to oxygen and moisture. Whole system is placed inside the fume hood to ensure safety.

Figure 3-1: (left) Schematic diagram and (right) actual experiment setup at Luminous! for semiconductor nanocrystals synthesis.

3.1.2 Synthesis of CdSe Nanocrystals in Organic Medium

Synthesis of colloidal cadmium selenide (CdSe) QDs is based on the hot injection method [84], in which one of the precursor solutions (e.g., trioctylphosphine selenium (TOP:Se) at room temperature is injected swiftly into the hot liquid that contains another precursor (e.g., cadmium oleate ($\text{Cd}(\text{OA})_2$). Such injection creates two effects: (a) additional selenium precursor alters the cadmium precursor solubility and (b) causes rapid drop in temperature of the liquid. The precursor reaches supersaturation stage in a very short time and allows nucleation to take place immediately. The number of nuclei formed at this stage depends on the concentration of the two precursors. Usually a larger number of nuclei formed during nucleation will result in smaller nanocrystal size, and due to the focusing effect, the size distribution of QDs is narrow. In contrast with CdTe synthesis in aqueous medium, which takes hours to complete, the reaction of cadmium selenide (CdSe) synthesis in organic medium is fast and the reaction time is relatively short (normally within 30 min)[57, 88, 96, 97].

For a typical synthesis of red CdSe QDs [98], cadmium oleate ($\text{Cd}(\text{OA})_2$), trioctylphosphine oxide (TOPO, 99%, ReagentPlus), hexadecylamine (HDA, 90%, Tech), and 1-octadecene (ODE, 90%, Tech) are added into a 3-neck flask. The mixture is first degassed in vacuum environment for 30 min to remove oxygen, moisture, and unwanted impurities, followed by filling the flask with argon gas to maintain inert gas environment. The solution temperature is then increased to 300 °C and, at the elevated temperature, the precursor solution

containing TOP:Se is injected rapidly into the high temperature solution to initiate the nucleation process. The solution temperature is maintained at 270~280 °C to promote the nanocrystals growth. After that, the reaction is stopped by injecting toluene into the flask to quickly reduce the solution temperature. Since TOP:Se is very sensitive to oxygen, the entire preparation and growth must be carried out in inert gas environment (Ar, N₂), or QDs will be oxidized, causing reduction of their quantum yield.

Figure 3-2: Flow-chart of CdSe synthesis.

3.1.3 Shell Formation Using Successive Ionic Layer Adsorption and Reaction

Developed by Peng's group in 2003 [99], successive ionic layer adsorption and reaction (SILAR) is one of the most widely used and effective techniques to overcoat wide bandgap shell materials (e.g., cadmium sulphide (CdS), zinc sulphide (ZnS)) around the cadmium selenide (CdSe) core. The principle behind SILAR is similar to atomic layer deposition (ALD), in which the deposition takes place in two subsequent steps using two types of reactants (anionic and cationic). In SILAR, the two precursors are injected alternatively at a lower temperature so that nucleation of the shell material is unlikely to happen and therefore attachment onto the CdSe core, forming half layer of the shell in each step is favored. Introducing the anionic and cationic precursors one at a time in alternating order, the shell growth is continued.

For a typical shell formation using SILAR method, the CdSe core nanocrystals which are dispersed in hexane, oleylamine (OLA, 90% tech) and 1-ODE were added into a 3-neck flask. Here oleylamine is used as the surface ligands, and 1-ODE serves as the non-coordinating solvent [100]. The solution is first pumped down at room temperature to remove unwanted solvents and impurities. Subsequently, it is filled with argon gas and further heated to 240 °C for shell precursor injections. The amount of injected precursor is calculated based on the number of the core nanocrystals and the amount needed to coat one monolayer around the CdSe core, strongly depending on the core size. The size of CdSe core is predicted using the first excitonic peak λ from the

absorption spectrum and the empirical fitting function reported by Peng *et al.* [101], as shown in Equation 3.3. Precise amount of cadmium precursor is first injected into the 3-neck flask and, after waiting for 10 min, sulfur precursor is injected [102]. The process of one monolayer formation takes about 30 minutes. Injections of cadmium and sulfur are repeated as many times as desired, forming the desired number monolayers of CdS surrounding the CdSe core.

$$Diameter_{CdSe} = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-3})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + 41.57 \text{ (nm)}$$

(3.3)

where λ is the first excitonic peak determined from the absorption spectrum. After shell formation, QDs exhibit a slight red shift in their emission spectrum, due to the increased effective nanocrystal size and increased dielectric medium. However, the quantum yield improves significantly as the wavefunctions of hole and electron are confined more in the core while surface traps are now passivated better by the shell.

Figure 3-3: Flow-chart of shell formation using SILAR method.

Figure 3-4: Transmission electron micrograph of CdSe/CdS core/shell QDs. The size of the QDs is 7.83 ± 0.83 nm.

3.1.4 Alloyed CdZnSeS Quantum Dots with Composition Gradient

Although CdSe/CdS core/shell QDs can achieve near unity quantum yield [103], the two-step synthesis method is time consuming and requires precise core purification. Developed by Bae *et al.* in 2008 [104], alloyed CdZnSeS QDs with a composition gradient can be made in a single-step synthesis where core and shell materials are loaded inside the 3-neck flask at the beginning. Due to different reactivity of precursors (Cd- and Se- precursors are more reactive than others), only CdSe core is formed at the nucleation stage while the remaining excess precursors are gradually attached onto the core during the growth of the QDs. As a result, the inner shell layers are Cd-rich while the outer shell layers are mainly Zn cations, forming alloyed core/shell QDs with a chemical composition gradient. Due to the gradient composition, lattice mismatch between CdSe and ZnS is relieved, surface traps are

minimized and the resulting alloyed CdZnSeS QDs therefore exhibit high PL quantum yield [6, 97].

For a typical alloyed CdZnSeS QDs synthesis, cadmium oxide, zinc acetate, oleic acid and 1-ODE are first loaded into a 3-neck flask and heated to 150 °C under vacuum environment for 20 min. After that, the flask is filled with argon gas and the temperature is further increased to 300 °C. At the elevated temperature, a certain amount of TOP:Se and TOP:S is injected into the 3-neck flask and the temperature is maintained at 300 °C for QD growth. The reaction takes 10 min to complete, and alloyed ZnCdSeS QDs with the composition gradient and soft barrier are obtained.

Figure 3-5: (left) Schematic diagram of the alloyed CdZnSeS QDs with a chemical composition gradient and (right) their corresponding energy diagram of alloyed CdZnSeS QDs.

Figure 3-6: Flow-chart of synthesize alloyed CdZnSeS quantum dots with composition gradient.

3.1.5 Purification of QDs

Purification of QDs is performed after the QD synthesis in order to obtain desired concentration as well as remove the unreacted precursors and excess ligands. For a typical cleaning process, the initial QDs are first precipitated by adding acetone and centrifuge at 5000 rpm for 5 min. Adding acetone will reduce the solubility of QDs in the mixture and therefore QDs will precipitate at

the bottom of centrifuge tube. A powerful centrifuger is used to accelerate this process. After centrifugation, the supernatant is discarded and the resulting bottom precipitates are redispersed in toluene. This process is repeated for 2 times to remove the excess ligands. The cleaned QDs solution is then filtered using 0.2 μm PTFE filter and stored in fridge to prevent degradation.

3.1.6 Quantum Dot Characterization

Photoluminescence quantum yield (QY) of QDs is important for the QD-LEDs since it directly affects the performance of the device. The QY of QDs is defined as the ratio of the total number of emitted photons from the QDs to the total number of absorbed photons by the QDs, as shown in Equation 3.4

$$QY = \frac{\text{photons}_{\text{emitted}}}{\text{photons}_{\text{absorbed}}} \quad (3.4)$$

An absorbed photon creates an electron-hole pair (exciton) inside the QD. Then the exciton can decay either radiatively or nonradiatively. Radiative decay implies that a photon is emitted at a longer wavelength during electron-hole pair recombination, and nonradiative decay can happen either via Auger recombination in which an extra hole or electron is excited to higher energy state, or Shockley–Read–Hall recombination where exciton energy is absorbed by the lattice and phonons are released. Therefore, the QY can also be rewritten as

$$QY = \frac{k_r}{k_r + k_{nr}} \quad (3.5)$$

where k_r is the radiative recombination rate and k_{nr} is the nonradiative recombination rate. It is obvious if the nonradiative rate k_{nr} is suppressed, we can get a perfect unity QY

$$QY = \frac{k_r}{k_r + 0} = \frac{k_r}{k_r} = 1 \quad (3.6)$$

QY of a sample can be determined by two methods: absolute quantum yield measurement and relative quantum yield measurement which relies on the comparison of the emission efficiency with a standard reference dye [105, 106].

The absolute quantum yield measurement is performed using a Hamamatsu Quantaaurus-QY PL quantum yield measurement system, and the system is shown in Figure 3-7. During measurement, the sample is placed inside a calibrated integrating sphere and excited using a Xenon light source. This method is fast and useful for thin film QY measurement compared to the relative quantum yield measurement method because most of the standard reference dyes require dissolving in particular solvents and they will not emit fluorescence in the powder form.

Figure 3-7: (left) PL spectrum of the excitation light source and QDs sample. (right) The actual Quantaaurus-QY PL quantum yield measurement system (image cortesy of Hamamatsu website [107]).

Alternatively, the QY of QDs in dispersion can be determined by a comparative method, in which the QD solution under test and a standard reference dye solution with a known QY are illuminated under the same excitation source, and the QY of the QD solution is retrieved by comparing the amount of the photons generated under excitation using the following relation:

$$QY_{QD} = QY_{ref} \frac{A_{ref}}{A_{QD}} \frac{F_{QD}}{F_{ref}} \left(\frac{n_{QD}}{n_{ref}} \right)^2 \quad (3.7)$$

where QY_{QD} and QY_{ref} are the quantum yield of the QD sample and the standard reference dye, respectively, A_{QD} and A_{ref} are the respective absorption of the QD sample and standard reference dye at the same excitation wavelength, F_{QD} and F_{ref} are the corresponding photon counts emitted by the QD sample and standard reference dye under the same excitation wavelength, n_{QD} and n_{ref} are

the refractive indices of the QD solution and standard reference dye solution, respectively.

Figure 3-8: (left) Absorption and (right) photoluminescence spectra of a QD sample under test and a reference dye (Rhodamine 6G).

For this measurement, a Shimadzu UV-1800 UV-Vis spectrophotometer, Shimadzu RF-5301PC spectrofluorophotometer, is used. For a typical measurement, QD sample and a standard reference dye are dissolved in particular solvents so that their absorbance is kept below 0.1 to prevent re-absorption among QDs, which could otherwise underestimate the actual QY value. After that, samples are placed inside the spectrofluorophotometer and excited by a light source with a very narrow spectral bandwidth at which both absorption spectra intercept. At this wavelength both samples have the same absorbance, therefore they can be cancelled out and the quantum yield formula is simplified to

$$QY_{QD} = QY_{ref} \frac{F_{QD}}{F_{ref}} \left(\frac{n_{QD}}{n_{ref}} \right)^2 \quad (3.8)$$

In order to obtain accurate measurement, the standard reference dye and solvent should have as high purity as possible and be freshly prepared every time before the measurement because reference dyes are organic materials which may easily degrade over time. In addition, both standard reference dye and QD sample should have as much spectral overlap as possible to minimise the error coming from the photodetector. Below are the standard reference dyes used in our lab to determine QY. There are other useful standard dyes that can be found in the literature [105, 106, 108, 109] and available in the market.

Table 3-1: Standard dyes used in our laboratory as reference for quantum yield measurement.

Standard dye	Solvent	Useful excitation range	Peak emission wavelength	Quantum yield
Coumarin 460	Dichloromethane	350 nm – 380 nm	445.0 nm	0.98
Fluorescein 27	0.1M NaOH	435 nm – 515 nm	532.5 nm	0.87
Rhodamine 6G	Ethanol	450 nm – 480 nm	565.0 nm	0.95
Rhodamine 101	Ethanol	530 nm – 580 nm	587.6 nm	1.00

Quantum yield measurement using the comparative method is widely used because of the equipment availability and its relatively simple procedure. However, solid film quantum yield measurement is always more challenging due to the lack of standard reference in the dry film condition.

3.2 Fabrication of QD-LEDs

The concept of QD-LED film architecture can be considered as stacking of different layers together, for examples, electron/hole injection layer and transport layers, emissive layer (active layer) and the electrodes. In this thesis, two widely used deposition techniques were used: (1) solution-based processing for polymer and colloidal QD deposition and (2) thermal evaporation method for depositing organic small molecule materials and metal electrodes. Typical device schematic of the fabricated QD-LEDs is shown in Figure 3-9.

Figure 3-9: Schematic diagram of a typical QD-LED, where the QD layer is placed at the emissive layers shown in this sketch.

3.2.1 Solution Process Method

Solution process method is favorable nowadays because of its low cost and high throughput. In contrast with physical vapor deposition, which operates under low pressure environment, solution process can be performed in ambient environment. Manufacturing cost can thus be reduced significantly since

expensive ultra-high vacuum chamber is not required in the fabrication process. Typical solution process techniques include spin-coating, dip-coating, layer-by-layer assembly, mist deposition and Langmuir-Blodgett technique. In this thesis, spin-coating technique is used to deposit colloidal QD and polymer transport layers.

Spin-coating is widely used in the microelectronic industry for photoresist coating. During the spin-coating process, solution containing target materials (colloidal QD/polymer) are first dropped, fully covering the substrate and then rotated rapidly at the desire rotation rate. Centrifugal force arises with the rotation and makes the precursor solution to spread over the entire substrate. Excess solution will then eject off from the substrate edge, leaving a thin film on the substrate. The process procedure of the spin-coating is illustrated in Figure 3-10.

Figure 3-10: Schematic diagram illustrates the spin coating process.

The thickness of the film is controlled by varying the precursor concentration, rotation speed, acceleration, and time, and the type of solvent used in the process. Typically higher speed, larger acceleration and longer spin time lead to thinner films, and using concentrated precursors and low boiling point solvents (dichloromethane, chloroform, chlorobenzene, hexane, etc.) can help to achieve thick films.

Selecting solvents and organic materials plays a significant role in this step. The structure of QD-LEDs consists of multiple thin film layers, and the emissive layer is chosen to be colloidal QDs, which can be dispersed in organic solvent such as toluene and hexane. In this case, it is essential for the underlying layer (hole transport layer) to withstand subsequent organic solvents. Most of the organic hole transport layers are dissolvable in toluene; therefore, they are not suitable in solution process. In our works, crosslinkable organic polymers such as poly(9-vinylcarbazole) (PVK), poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-secbutylphenyl))diphenylamine)] (TFB), and poly(N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)-benzidine) (poly-TPD) are used as the hole transport layers. Such polymers, after a crosslinking process via annealing or ultraviolet treatment, are resistant to toluene and hexane corrosion hence they are widely used in the QD-LEDs [4, 66, 110].

Figure 3-11: (left) High resolution field-emissive scanning electron micrograph (FE-SEM) showing a close packed film of QDs deposited on top of poly-TPD, before deposition of the electron transporting layer. (right) Photo shows the electroluminescence of green QD-LEDs.

3.2.2 Thermal Evaporation Technique

Thermal evaporation is one of the physical vapour deposition (PVD) techniques widely used in industry to deposit thin films. Target material (organic small molecule or metal oxide powder) is placed inside crucible (quartz/alumina) or tungsten boat and heated up to the materials' boiling point. At the desired temperature, target materials evaporate and create vapour cloud inside the chamber. The vapour will pass through the deposition chamber and sublime onto the substrate. In order to achieve high-quality thin film, this technique requires very high vacuum of 10^{-5} torr. Deposition rate and film thickness can be monitored using quartz microbalance in real time. For organic small molecule and metal cathode deposition, the deposition rate is maintained at $0.1 \text{ \AA s}^{-1}$ to ensure film flatness. Two sets of masks are used to define the area of organic material deposition and the metal contact.

Figure 3-12: (top) Schematic diagram of the organic material thermal evaporator and (bottom) the electrical controller and the deposition chamber of the organic deposition tool.

3.3 QD-LED Characterization

After QD-LED fabrication, the devices are kept in N₂ glove box, which maintains the oxygen and water vapour level below 1 ppm. This is to prevent device degradation as most of the organic materials are sensitive to oxygen and moisture. All the device measurements were taken in a dark room under standard room environment, without device encapsulation. In order to minimize all the possible degradation, devices are characterized immediately after the fabrication.

Two important characteristics of QD-LEDs are (a) electronic and (b) optoelectronic properties of the devices. We will discuss in detail of these electrical and optical characterizations in the following parts.

3.3.1 Electronic characterization

Electronic measurement of QD-LEDs involves the current-voltage (I-V) characterization. The I-V characteristics are taken using a YOKOGAWA GS610 source measurement unit, which is controlled by home-built LabView program. During measurement, the measurement unit applies a varying voltage across the device and measures the current passing through the device point by point. From the I-V curve we can find out one of the key characteristics of QD-LED performance, the turn-on voltage, which is taken as the voltage required for the devices to generate luminance of 1 cd m^{-2} [111, 112].

3.3.2 Optical Characterization

Measurement of QD-LEDs luminance and emission spectra were performed using a LabView-controlled Konica-Minolta LS-100 luminance meter and PhotoResearch SpectraScan PR705 spectroradiometer. The devices EQE was calculated based on the technique described by Forrest and his colleagues using the test sample's brightness, current and electroluminescence spectrum, with the valid assumption that emission profile of the devices is Lambertian [113]. Details of the calculations are described in the following part.

Optical light is electromagnetic radiation with a range of frequency and energy, as shown in Figure 3-13. In this thesis we only focus on the range

falling in the visible window (400 - 700 nm), which can be perceived by the human eye.

Figure 3-13: Different range of electromagnetic wave radiation.

Although human eye can recognize light within the visible window, in general, the eye sensitivity to different wavelength of light source is different. For example, under the same light intensity, green light is always perceived to be brighter than other wavelength light sources. Figure 3-14 shows the photopic response of human eye, also known as the luminosity function. It can be seen that human eye is very sensitive to the green emission (peak at 555 nm), while less sensitive in the ranges longer than 650 nm and shorter than 450 nm. For lighting purpose, it is more meaningful to characterize the light source with respect to the luminosity function.

Figure 3-14: Luminosity function of the human eye response [14, 114].

The perceived brightness of a light source is measured in term of luminance, which is the luminous flux received by the human eye from a particular solid angle. It has the SI unit of candela per square meter (cd m^{-2}). It can be calculated based on the EL spectrum and the luminosity function [115], as shown in Equation 3.9:

$$\text{Luminance } (L_v) = 683 \left(\frac{\text{lm}}{\text{W}} \right) \int_{360 \text{ nm}}^{830 \text{ nm}} I(\lambda) V(\lambda) d\lambda \quad (3.9)$$

where L_v is the luminance of the light source, $I(\lambda)$ is the radiant intensity of the light source, and $V(\lambda)$ is the normalized luminosity function.

From the luminance (L_v) and current density (J), one can deduce the current efficiency (CE) of the device. It is used to describe how well is the charge injection utilized in the LED devices. It is defined as the ratio of luminance to the current density, as given below:

$$\text{Current Efficiency (CE)} = \frac{\text{luminance}}{\text{current density}} = \frac{L_v(\frac{cd}{m^2})}{J(\frac{A}{m^2})} \quad (3.10)$$

Under the same luminance, to achieve high current efficiency, the current density must be low, meaning that more of the injected charges successfully form excitons and recombine radiatively (i.e., emit photons). If there is leakage between the interfaces, the current density will increase and reduce the current efficiency.

In addition, we can determine the power efficiency (PE) or luminous efficacy of the device using luminous flux and the input power with the assumption that the LED illumination profile is Lambertian, shown by the following equation:

$$\text{Power Efficiency (PE)} = \frac{\text{luminous flux}}{\text{input power}} = \frac{\pi L_v(lm)}{V \times J(W)} \quad (3.11)$$

where L_v is the measured luminance, V is the operating voltage and J is the current density. From this relation we can find that the operating voltage must be small to achieve high power efficiency device.

Ideally a LED should emit one photon for every injected electron-hole pair. However, in reality, due to various nonradiative decay routes, the

conversion of carriers to photons is less efficient. For that, internal quantum efficiency (IQE) is defined as the ratio of the emitted photons to the injected electrons into the LED:

$$\begin{aligned}\eta_{int} &= \frac{\text{no. of photons emitted from the active region}}{\text{no. of electron injected into the LED}} \\ &= \frac{\int \frac{I_{\text{active region}}(\lambda)}{h\nu} d\lambda}{\frac{I}{e}}\end{aligned}\tag{3.12}$$

where $I(\lambda)$ is the optical power emitted from the active region, h is the Plank's constant, ν is the frequency of the emitted wavelength, I is the injection current, and e is the charge of an electron. Ideally η_{int} is unity, which means that every injected electron will generate a photon.

LED devices are commonly fabricated on transparent substrates (soda lime glass, sapphire, etc.) to allow visible light to pass through (unless in an inverted structure). The transparent substrates generally have refractive indices much higher than the air ($n = 1$). When light emitted from the active region, they have to travel through a stack of organic and inorganic materials which have different refractive indices. At the interface of two media, part of light will be reflected back and most will leak into the layer. To study the ability of light escape from the device, the light extraction efficiency ($\eta_{\text{extraction}}$) is defined as

$$\begin{aligned}
\eta_{\text{extraction}} &= \frac{\text{no. of photons emit to the free space}}{\text{no. of photons emit from the active region}} \\
&= \frac{\int \frac{I_{\text{extracted}}(\lambda)}{h\nu} d\lambda}{\int \frac{I_{\text{active region}}(\lambda)}{h\nu} d\lambda}
\end{aligned}
\tag{3.13}$$

where $I_{\text{extracted}}(\lambda)$ is the optical power extracted and received in the free space. $\eta_{\text{extraction}}$ becomes unity when all generated photons at the active region are successfully extracted out from the device.

Combining both the internal quantum efficiency η_{int} and the light extraction efficiency $\eta_{\text{extraction}}$, we obtain the external quantum efficiency η_{ext} , which describes how efficient a photon will escape from the device when a charge is injected into the device.

$$\begin{aligned}
\eta_{\text{ext}} &= \frac{\text{no. of photons emitted into the free space}}{\text{no. of electrons injected into LED}} \\
&= \eta_{\text{int}} \times \eta_{\text{extraction}} \\
&= \frac{\int \frac{I_{\text{extracted}}(\lambda)}{h\nu} d\lambda}{\frac{I}{e}}
\end{aligned}
\tag{3.14}$$

There are few parameters that can be extracted from the device electroluminescence spectrum, for example, color coordinates of the emission spectrum. Being standardized and released by The International Commission

for Illumination Commission (Commission Internationale de l'Eclairage, CIE) in 1931, color spectrum is related to color coordinates, which can be determined using the CIE standard observer color matching functions, as shown in Figure 3-15.

Figure 3-15: CIE 1931 standard observer colour matching functions [14, 114].

Based on the sample spectrum and the color matching functions, we can obtain the tristimulus values, X, Y, Z based on the equations below:

$$X = \int_{360\text{ nm}}^{830\text{ nm}} I(\lambda) \bar{x}(\lambda) d\lambda \quad (3.15)$$

$$Y = \int_{360\text{ nm}}^{830\text{ nm}} I(\lambda) \bar{y}(\lambda) d\lambda \quad (3.16)$$

$$Z = \int_{360\text{ nm}}^{830\text{ nm}} I(\lambda) \bar{z}(\lambda) d\lambda \quad (3.17)$$

where $I(\lambda)$ is the spectral power distribution received from the sample. In fact, the color matching function y is the photopic luminosity function; therefore, value Y is also known as the luminance of light source. Also with the following conversion, we can display the CIE 1931 chromaticity coordinates on the CIE diagram.

$$x = \frac{X}{X+Y+Z} \quad (3.18)$$

$$y = \frac{Y}{X+Y+Z} \quad (3.19)$$

$$z = \frac{Z}{X+Y+Z} \quad (3.20)$$

It is clear that x, y, z will sum up to 1. We can also use Equation 3.21 to obtain the z value.

$$z = 1 - x - y \quad (3.21)$$

Since the z chromaticity value does not contain additional information, it is sufficient to use x and y values to describe the color of the sample. Figure 3-16 shows the CIE 1931 chromaticity diagram.

Figure 3-16: CIE 1931 chromaticity diagram [14, 114].

Color temperature (CT) of a light source is defined by the temperature of blackbody emission that has the same coordinate to the light source. The unit of color temperature is in kelvin (K).

By plotting the color coordinates of the blackbody emission at different temperatures onto Figure 3-13 and connecting them together, one can get the

Planckian locus. If the CIE 1931 color coordinate of the light source does not fall on the Planckian locus, correlated color temperature (CCT) was used instead to describe the color appearance of that particular light source. Correlated color temperature of a white light source determined by the color temperature of the Planckian black body whose color coordinate is closest to that of the given white light source.

Colour rendering index (CRI) of a white light source is a measure of its ability to render a physical object colors "realistically" or "naturally" as compared to a reference (either incandescent light or daylight) with same CCT.

As a guideline, for indoor lighting applications, the color coordinates should be very close to the Planckian locus, so that they have high color rendering index (CRI). However, for display purpose, the color coordinates of each component should be close to the perimeter in order to represent the largest available color span.

CHAPTER 4: White Light Generation of QD-LED using Loosely-packed QD Film

In this chapter we demonstrate colloidal quantum dot light-emitting diodes (QD-LEDs) with broad emission spectrum that covers the entire visible window. In the first part we provide background and objective of the research, followed by the experiments toward white light generation. The final part will present the results and discussion about the working mechanism of our QD-LEDs.

4.1 Introduction

Colloidal quantum dot light-emitting diodes (QD-LEDs) have caught considerable interest in optoelectronic applications including lighting solutions with high color rendering index (CRI) and thin film flat-panel displays with high color purity and wide color gamut [48, 57, 116-118]. The electroluminescence spectrum of QD-LEDs is generally narrow and can be easily tuned from blue to red by varying the size and composition of the dots. To date, the performance of monochrome QD-LEDs are comparable to the organic light-emitting diodes (OLEDs) [62, 67] and GaN-based LEDs [67]. However, white QD-LEDs have rarely been reported. In fact, it is difficult to obtain high-performance white QD-LEDs by simply mixing blue-, green-, and

red-emitting QDs. When the inter-distance between dots are sufficiently close, blue QDs tend to transfer their energy nonradiatively to the QDs that have longer wavelength emission (e.g. red or green QDs). In addition, blue QD is more difficult to be electrically-excited compared to green and red QDs [45]. Currently, realization of high-performance white QD-LEDs has been reported based on the combination of organic molecules and QDs emission [119, 120]. However, much work is needed in hybrid QD-LED research for improved performance.

In this chapter, we demonstrate green-emitting QD-LEDs using alloyed CdZnSeS quantum dots with a composition gradient, achieve maximum brightness of 9400 cd m^{-2} and low turn-on voltage of 4.20 V. Then, by adapting Yang *et al.* protocol, we sandwiched a loosely packed QD-layer between poly-[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine] (poly-TPD) hole transporting layer (HTL) and the 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) electron transport layer (ETL) to demonstrate white QD-LED [121]. The white emission consist of blue emission from poly-TPD HTL, green emission from QD active layer and red emission from the exciplex emission between poly-TPD and TPBi. The resulting white QD-LEDs consist of show a good photometric performance with a high CRI of 95 and a moderate low correlated color temperature (CCT) of 4098 K.

4.2 Experimental Session

4.2.1 QD Synthesis and Purification

We synthesized green-emitting alloyed cadmium zinc selenide sulphide (CdZnSeS) quantum dots (λ_{peak} 510 nm) with a composition gradient using the protocols published in the literature [6, 97, 104, 110] as follows: 0.2 millimolar cadmium oxide (CdO) and 4 mmol of zinc acetate dihydrate ($\text{Zn}(\text{Acet})_2 \cdot 2 \text{H}_2\text{O}$), 7 mL of oleic acid (OA) and 20 mL of 1-octadecene (1-ODE) were added into a 50 mL 3-neck flask and undergone a degassing process at 100 °C in vacuum environment for 30 min. Subsequently, the flask was filled with ultra-pure argon gas (5N grade) so that the pressure inside the flask was maintained at 1 atm. The temperature was then increase to 300 °C. After that, 0.1 mmol of selenium (Se) powder and 4 mmol of sulphur (S) were mixed with 3 mL of tri-octylphosphine (TOP) and injected into the flask. The nucleation of the QDs was started and the solution temperature was maintained at 300 °C for 10 min to carry out the alloyed CdSeZnS nanocrystal growth.

The as-synthesized QDs were purified by precipitation/dispersion method discussed in the previous chapter and redispersed into toluene with a concentration 10 mg mL⁻¹. The QD solution was characterized to have a quantum yield of 40% through relative quantum yield method. The standard dye used for the comparison was fluorescein-27 in 0.1 M NaOH solution, which has a quantum yield of 87% with an 502 nm peak emission [105].

4.2.2 Device Fabrication and characterization

Soda lime glass substrate coated with ITO (sheet resistance of $30 \Omega/\square$) was first patterned by lithography and etching process, and then went through a routine cleaning procedure, which includes ultrasonication of substrate in detergent (decon 90), de-ionized (DI) water, acetone and ethanol. The substrate was placed in oven overnight at 80°C for drying the solvents. The substrates were treated with 5 min O_2 plasma before loading into the glovebox for deposition to improve the surface morphology. First, conductive polymer PEDOT:PSS was spin-coated at a speed of 3000 rpm and followed by 30 min annealing in N_2 atmosphere at 100°C . After that, poly-TPD and QD solutions were spin-coated consecutively to create a HTL and an active layer, respectively. The samples were then loaded into deposition chamber for TPBi, lithium fluoride (LiF) and Al deposition at a rate of $1 \text{ \AA s}^{-1}$. The thickness of the organic film was monitored in real time by quartz crystal microbalance. The QD-LED devices has an effective area of 9 mm^2 .

4.2.3 Device Measurement

A PhotoResearch SpectraScan PR705 spectroradiometer was used for measuring the luminance and emission spectra of the fabricated QD-LEDs, while the device electrical characteristics were obtained concurrently using a Yokakawa GS610 source measurement unit. Details of measurement and calculation were described in Chapter 3.

4.3 Results and Discussions

The device studied here consists of ITO (120 nm)/PEDOT:PSS (60 nm)/poly-TPD (30 nm)/QD emissive layer (20 nm)/TPBi (35 nm)/LiF (0.6 nm)/Al (150 nm) and their corresponding energy band diagram is shown in Figure 4-1. For the device, PEDOT:PSS is served as the hole injection layer (HIL), poly-TPD and TPBi are hole and electron transport layers used to transport holes and electrons, respectively, to the QD emissive layer. LiF, together with Al are served as the cathode. Figure 4-2 shows the QD-LED emission spectrum recorded at the current density of 222 mA cm^{-2} . Figure 4-2 shows green emission peak located at 516 nm with a linewidth of 40 nm. Weak blue emission is also observed from the poly-TPD. This blue emission can be adjusted by changing the hole-transporting layer (poly-TPD) and electron transporting layer (TPBi) thicknesses. However, the blue poly-TPD emission is hardly eliminated due to the large energy barrier between the highest occupied molecular orbital (HOMO) of poly-TPD and QDs valence band. Injected holes were blocked at the poly-TPD/QD interface and emit light when they recombine with electrons injected from the cathode.

Figure 4-1: (left) Device structure of the studied QD-LED, (right) correspondent band diagram of the studied QD-LED.

Figure 4-2: Electroluminescence spectrum of the studied QD-LED. The emission spectrum consists of poly-TPD emission (430 nm peak) and QD emission (525 nm peak)

Figure 4-3 presents the performance of the optimized QD-LEDs. The device was turned-on at 4.20 V. Here the turn-on voltage is the operating voltage with a light output of 1 cd m^{-2} . The maximum luminance of the optimized QD-LEDs is close to 5000 cd m^{-2} and the external quantum efficiency (EQE) reaches 0.92% under a current density of 55.56 mA cm^{-2} .

Figure 4-3: Luminance (L) and current density (J) versus voltage (V) characteristics of the studied QD-LED.

In order to examine the blue emission from our QD-LED, we fabricated QD-free LEDs for comparison. The structure of the QD-free device is similar to the QD-LED except for the QD layer. Specifically, it consists of ITO (120 nm)/PEDOT:PSS (60 nm)/poly-TPD (30 nm)/TPBi (35 nm)/LiF (0.6 nm)/Al

(150 nm). For this device, the injected electrons and holes are expected to meet at the interface of poly-TPD/TPBi interface to form excitons that will then recombine and emit light. The emission spectra of the QD-free LED under different levels of bias voltage are shown in Figure 4-4. Interestingly, beside the blue poly-TPD emission, we also observe a red component having a emission peak around 620 nm on the emission spectra. Based on the band diagram, we found that the energy gap between the HOMO of poly-TPD (-5.2 eV) and the LUMO of TPBi (-3.2 eV) is 2.0 eV, which can correlate to the red emission component. Therefore, we attribute the red emission to the exciplex emission from the donor and the acceptor, which are in the excited state and the ground state, respectively. A similar exciplex emission formed between the hole transport layer and polyfluorenes was previously reported by Sun *et al.* [122].

The exciplex emission of the QD-free devices is voltage-dependent. Under low bias voltage, the EL spectrum is dominated by poly-TPD emission as most of the excitons are formed inside the bulk poly-TPD film. When the bias voltage increases, the recombination zone of the excitons shifts toward to the interface of poly-TPD and TPBi, therefore the relative contribution of exciplex emission increases.

Figure 4-4: Electroluminescence spectra of the QD-free device under different levels of applied voltage bias.

White light emission can be achieved by combining the blue poly-TPD emission, red exciplex emission from charge-transfer exciplexes formed at the poly-TPD/TPBi interface and the green QD emission. In order to promote the red exciplex emission, we purposely reduce the QD coverage during the fabrication so that there is some space left between the adjacent QDs to allow a direct contact of poly-TPD and TPBi. The schematic diagram of the device is shown in Figure 4-5.

Figure 4-5: (Left) Device schematic of a QD-LED with loosely packed QD emissive layer. (Right) Atomic force micrograph (AFM) image of the studied loosely-packed QD film.

The loosely packed QD layer was obtained by reducing the concentration of QDs in starting solution and increasing the spin-coating rate. Figure 4-5 shows the atomic force micrograph (AFM) of a loosely-packed QD layer deposited onto a 30 nm thick poly-TPD layer. It can be clearly seen that the coverage of QDs is not complete and there are open spaces between the dots. The LED spectrum recorded at the bias voltage of 12 V exhibits a broadband emission over the entire visible window, and the main emission peaks can be observed in the spectrum, as shown in Figure 4-6. The white light of the QD-LED is characterized to have a high colour rendering index (CRI) of 89 at a correlated color temperature (CCT) of 6752 K. The CIE 1931 coordinates of the device's light is (0.31, 0.30), which lies on the Planckian locus close to the white point (D65) of various color space standard (0.31, 0.32), making it a suitable backlight source for flat panel displays.

Figure 4-6: Emission spectrum of the white light QD-LED at an operating voltage of 12 V.

Figure 4-7: Emission spectra of the QD-LED under different voltage bias levels.

The spectral power distribution of the white QD-LEDs can be tuned easily by changing the bias voltage. Figure 4-7 shows the change of EL spectrum with respect to voltage bias. By increasing voltage, we observe a rapid increase of the red exciplex emission and QD emission in the EL spectrum relative to the initially dominant blue component. This indicates that the exciton formation zone is shifted toward the QDs and poly-TPD/TPBi interfaces. The CIE 1931 colour coordinates for the QD-LEDs under different voltage bias levels have been calculated and presented in the CIE 1931 colour diagram in Figure 4-8. The chromaticity calculation suggests that it is possible to tune the desired colour coordinates of the three emissive components in our QD-LED by adjusting the bias voltage, if brightness variation of light is not a concern.\

Figure 4-8: CIE 1931 chromaticity coordinate diagram and the coordinate of the QD-LED at different voltage biases.

4.4 Conclusion

In summary, colloidal QD-LEDs with efficient green emission have been fabricated in our study. Additionally, our carefully spin-coated loosely-packed QD layer allows for partial contact of poly-TPD and TPBi, creating additional recombination zones in the device. The resulting white QD-LED consisting of blue, green and red components from the poly-TPD, green emitting QDs, and the exciplex formed at the interface between the poly-TPD and TPBi, respectively, has been demonstrated with a high colour rendering index of 89. Realistic progress towards the practical application in white QD-LEDs has been achieved. Furthermore, the successful realization of the ternary complementary white QD-LEDs may provide a promising strategy for future design and fabrication of high-performance optoelectronic devices with multi-colour components.

CHAPTER 5: Improving QD-LEDs

Performance by Sandwiching Quantum Dots between Two Hole Transporting Layer

In this chapter, we discuss hybrid, non-inverted quantum dots light-emitting diodes (QD-LEDs) with their quantum dots (QDs) placed between two hole transport layers (HTLs) [110]. The studied devices with additional HTLs can obtain up to 5-fold improvement compared to the conventional device structure which is the reference device for our study. The parasitic blue poly(4-butylphenyl-diphenyl-amine) (poly-TPD) emission that is commonly observed in the reference structure due to the excess electrons leaking towards the HTL is not observed in the proposed device. With an extra HTL in the electron transportation path, 97% of the excitons formed in the QD layer in the proposed device, while 3% of the excitons take place in the organic charge transport layer. It is found that better exciton confinement in the QDs' zone is one of the key factors for the device external quantum efficiency enhancement. In this chapter, the first section will give a brief introduction and motivation of this work, followed by the experimental part and the next section will discuss about the results. The last section will summarize and conclude the work of this chapter.

5.1 Introduction

Up to the time of our research here in 2012, high-brightness QD-LEDs had been successfully demonstrated with luminance levels exceeding 10000 cd m^{-2} [43, 56, 123], and peak external quantum efficiencies (EQE) over 2.7% (at $\lambda_{\text{peak}} \sim 600 \text{ nm}$) [44]. Though QD-LEDs have recently made a breakthrough to boost up the EQE and brightness to 18% [67] and brightness exceeding 50000 cd m^{-2} [43, 67], respectively, the device performance is still low for the QD-LEDs where double-sided organic charge transport layers (CTLs), i.e., hole transport layer (HTL) and electron transporting layer (ETL), sandwich the QD emissive layer between them. Although the electrons and holes are expected to form excitons inside the QDs and recombine radiatively for light generation, the energy band of the QDs in fact creates a more preferable injection path way for electrons than for holes. Only a small amount of injected holes can overcome the large energy barrier and be injected into the QDs, whereas excess electrons could leak toward the organic hole transport layer and contribute to parasitic polymer emission, thus effectively reducing the efficiency.

In this chapter, we present that placing QDs inside HTLs can effectively improve the device performance of a non-inverted device structure. This proposed device architecture yields over 5 times improvement in terms of EQE in the best optimized device, as compared to the reference device, in which QDs are deposited between the ETL and HTL. We attributed the improvement in EQE to the better charge balance inside the QDs. Also, it is found that the

exciton formation is now well confined in the QD layer and the Förster resonance energy transfer (FRET) from the CTLs to the QDs is minimum in the proposed device structure. The best device using this architecture reaches an EQE level of 3.14% at a peak emission wavelength of 512 nm with a minimal efficiency roll-off. To our knowledge this is the highest reported value for non-inverted structures using double sided organic charge transport layers. [8, 44, 56, 97].

5.2 Experimental Section

5.2.1 QD Synthesis and Purification

We used typical Schlenk line method to synthesize alloyed CdZnSeS quantum dots with a composition gradient, developed by Bae *et al.* [6, 97, 104]. For green-emitting CdSeZnS QDs with an emission peak of 510 nm, cadmium oxide (CdO, 0.1 mmol) and zinc acetate ($\text{Zn}(\text{Acet})_2$, 4 mmol), serving as Cd and Zn source, respectively, were added into a clean 3-neck flask, followed by the addition 5 mL of oleic acid (OA) ligand and 20 mL of 1-octadecene (1-ODE) non-coordinating solvent. The 3-neck flask was connected to the Schlenk line and heated to 100 °C under vacuum environment. The cadmium oxide and zinc acetate will react with oleic acid and form cadmium oleate ($\text{Cd}(\text{OA})_2$) and zinc oleate ($\text{Zn}(\text{OA})_2$). Then, the reactor flask was flowed with high purity nitrogen gas and further heated up to 300 °C. At this temperature, tri-octylphosphine (TOP, 2 mL) containing selenium (Se, 0.1 mmol) and sulphur (S, 3 mmol) was injected into the flask quickly, and the reaction solution was kept at 300 °C for

10 min to promote the nanocrystal growth. Following this step, the alloyed CdZnSeS quantum dots with a composition gradient were formed and the solution was cooled down to room temperature to stop the synthesis.

The excess ligand and unreacted materials in the QD crude solution were removed by standard precipitation/redispersion process as discussed in chapter 3. The QD solution was characterized using the reported method of comparing the fluorescence intensities with a standard reference dye and found to have quantum yield around 50%. The quantum yield value has been confirmed using absolute PL quantum yield measurement system and presented in Figure 5-1.

Figure 5-1: Quantum yield (QY) of the green-emitting quantum dots used in our experiments under different excitation wavelengths. The quantum efficiency was characterized by Hamamatsu Quantaurs-QY PL quantum yield measurement system. Reprinted with permission from Reference [110]. Copyright 2013 American Chemical Society.

5.2.2 Device Fabrication and Measurements

The patterned ITO glass (with a sheet resistance of $30 \Omega/\square$) was first cleaned using a routine procedure including consecutive ultrasonication of glass substrates in the detergent, deionized (DI) water, acetone and ethanol bath and then drying in the oven at 80°C overnight before using them in device fabrication.

Before loading the ITO substrates into the oxygen-free glove box, the ITO substrates were treated with a 5 min O_2 plasma to make the ITO surface hydrophilic. First, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) was spin-coated onto the ITO surface at a speed of 3000 rpm, followed by 30 min annealing process in an N_2 glove box. After that, 30 nm of poly-TPD HTL was deposited on top of the PEDOT:PSS. Heat was applied afterward so that the poly-TPD HTL is undergone cross-linking process. Subsequently, the QD active layer was then coated at a speed of 2000 rpm and cured for 30 min at 150°C . Following that, samples were loaded into a deposition chamber for the HTL (either 4,4',4''-tris-(carbazol-9-yl)triphenylamine (TCTA), 4'-bis(carbazol-9-yl)-biphenyl (CBP), N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'diamine (NPB) or 4-butylphenyl-diphenyl-amine (TPD)), electron transport layer (1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene, TPBi), electron injection layer (lithium fluoride, LiF), and cathode (aluminium, Al) deposition. The active area of each device is 9 mm^2 .

The electroluminescence spectra of the QD-LEDs were obtained using a PhotoResearch SpectraScan PR705 spectroradiometer and the electrical performance was recorded using a Labview-controlled Yogakawa GS610 source measurement unit. Details of measurement and calculation were described in chapter 3.

5.3 Results and Discussion

The reference and proposed new QD device schematics along with their corresponding energy band diagrams are shown in Figure 5-2. The structure of the reference QD device is adapted from the reported literature [8, 43, 44, 97], which consists of glass substrate/ITO (120 nm)/PEDOT:PSS (60 nm)/poly-TPD (30 nm)/QDs film (20 nm)/TPBi (35 nm)/LiF (0.5 nm)/Al (120 nm). In the reference QD device, poly-TPD and TPBi serve as HTL and ETL to inject holes and electrons, respectively, into the QD layer and recombine radiatively. However, from the energy band diagram shown in Figure 5-2, it is clear that the injected holes would face a large energy barrier of 1.9 eV between the highest occupied molecular orbital (HOMO) of poly-TPD and the valence band of the QDs. In contrast, the TPBi's lowest unoccupied molecular orbital (LUMO) and the QDs' conduction band are well aligned. This implies that there is no barrier to stop electron injection. This imbalance of band alignment results in injecting electrons into QD is easier than injecting holes, and causes a certain amount of excitons to recombine outside the QD layer. Furthermore, excess electrons

accumulate in the QD layer and charge the QDs, which promote Auger recombination process and reduce radiative recombination efficiency. This is the well-known charge imbalance issue of the conventional QD-LEDs and slowing down the electron injection into QD layer can be one of the solutions. The low electron mobility of HTL is utilized in this study to slow down the electron injection to the QD layer. In our proposed device, another HTL is placed between the QD and ETL, as shown in Figure 5-2(a).

Figure 5-2: (a) Schematic diagrams and (b) their corresponding energy band diagrams of the reference device and proposed device structure. For the reference device, quantum dots are deposited between the HTL and ETL (left) and for the proposed device structure, additional HTL is added between the QD layer and

ETL (right). Reprinted with permission from Reference [110]. Copyright 2013 American Chemical Society.

The reference and proposed QD devices are characterized for current density and luminance versus voltage (J-L-V) performance. Their results are shown in Figure 5-3. The proposed device uses a well-studied organic material, TCTA, between the QD layer and ETL to limit the electrons injected into QD. The turn-on voltages are measured to be 6.1 and 6.5 V, and the resulting maximum brightness levels are 2834 and 1011 cd cm^{-2} for the devices with and without the TCTA layer, respectively, showing significant improvement in brightness from the proposed device with respect to the reference.

Figure 5-3: Luminance-current density-voltage (L-J-V) characteristics of the QD devices with and without additional TCTA HTL, showing improvement on device brightness. Reprinted with permission from Reference [110]. Copyright 2013 American Chemical Society.

Figure 5-4 depicts the electroluminescence spectra of the studied QD-LEDs at a current density of 22.2 mA cm^{-2} . This clearly shows a notable improvement of the QD-LED performance from the device with the TCTA HTL. Compared to the reference device, the proposed device with the QD layer sandwiched between poly-TPD and TCTA obtained over 3-fold enhancement in the overall brightness and 5 times brightness enhancement at the peak emission wavelength (510 nm). In addition, our device also suppresses the blue emission, which is commonly found in the conventional device architecture, and the spectrum is shown in the inset of Figure 5-4. This blue emission due to the poly-TPD HTL layer is the evidence that excess electrons bypass the QD layer and leak towards the HTL. The electrons recombine with the holes in the poly-TPD and emit blue light. Therefore, it can be concluded that better charge balance in the QD layer has been achieved with the addition of TCTA, in which the injected electrons into QDs are reduced. This conclusion supports our previous hypothesis.

Figure 5-4: Reference and proposed device electroluminescence spectra under a current density of 22.22 mA cm^{-2} (inset) zoom-in of the EL spectrum in blue region. Reprinted with permission from Reference [110]. Copyright 2013 American Chemical Society.

We then fabricated a series of QD devices with different TCTA thicknesses to further study the effect of TCTA on the device performance. The current density versus voltage (J-V) characteristic is shown in Figure 5-5. The operating voltage of the QD device increases with the TCTA thickness, which is mainly due to the low electron mobility of TCTA ($<10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and the energy barrier caused by the TPBi/TCTA interface [124]. The device now requires a higher voltage bias to inject the same amount of charges into the QD layer.

Figure 5-5: Current density-voltage (J-V) characteristics of the devices with different thickness (0-30 nm) of TCTA used as additional HTL in the electron injection side. The turn-on voltage increases gradually with the addition of TCTA. Reprinted with permission from Reference [110]. Copyright 2013 American Chemical Society.

Figure 5-6 presents the device EQE versus current density (EQE-J) characteristics for the QD devices given in Figure 5-5. The reference device's performance (without TCTA) is also given in the same figure for comparison. It is obvious that device with a 20 nm thick TCTA exhibits the optimum performance among all fabricated devices. In addition, their EQE roll-off is comparable to the previous literature [8]. This finding suggests that the charge balance inside the QD layer was optimized at 20 nm. This device obtained a maximum level of brightness of 26370 cd m^{-2} at 333 mA cm^{-2} . The highest EQE, current conversion efficiency and the power conversion efficiency

measured from this structure are 3.14%, 8.7 cd A⁻¹ and 4.4 lm W⁻¹, respectively. In contrast, the reference device reaches levels of only 0.59%, 1.7 cd A⁻¹ and 0.8 lm W⁻¹, respectively, under the same current density.

Figure 5-6: External quantum efficiency versus current density (EQE-J) characteristics for the QD devices using 0-30 nm of TCTA HTL. The device EQEs improve consistently with the TCTA addition. The EQE reaches the maximum value with 20nm thick TCTA. Reprinted with permission from Reference [110]. Copyright 2013 American Chemical Society.

The effects of other HTL materials on the device performance were studied. Three widely-used hole transport materials, CBP, NPB, TPD, were used in this study. The electroluminescence spectra of the devices in this study are shown in Figure 5-7, and the enhancement factor, i.e. number of fold enhancement in the QD emission compared with the reference QD-LED structure (no HTL addition), is plotted in the inset. The devices with QDs

sandwiched between HTLs shows EQE improvement consistently. Comparing among four sets of devices, the device with TCTA showed better performance than other HTLs. The electron mobility of NPB, TPD and CBP are four order higher than the TCTA (6×10^{-4} , 9×10^{-4} , 3×10^{-4} , and $< 10^{-8}$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively) [124-126]. Devices using the other three HTLs would not be able to block excess electrons as efficiently as TCTA. More electrons can be injected into the QD layer and the charge balance could not be optimized in this layer, therefore resulting in low device performance.

Figure 5-7: Electroluminescence spectra of the devices using different HTLs. The inset shows the enhancement factor of the QD emission obtained in the proposed device structure using different HTL materials, in comparison to the reference device structure. The emission spectra were measured under the current density of 1 mA cm^{-2} . Reprinted with permission from Reference [110]. Copyright 2013 American Chemical Society.

As discussed in the previous chapter, the QD emission arises from four mechanisms, which are the optical excitation, FRET, direct charge injection and

field-induced QD-ionization. The thin QD layer and low biasing voltage lead to low efficiency of the optical excitation and field-induced QD-ionization mechanism. Anikeeva *et al.* also suggested that the emission route of this QD device architecture is mainly contributed by the direct charge injection and the FRET mechanism [52]. Although the charge is well balanced in the QD layer, the device performance improvement observed here may also come from the FRET process, in which excitons are first formed in the organic semiconductor (i.e., TCTA, NPB, TPD or CBP) and transfer their energy nonradiatively to the QDs [8].

Figure 5-8: Emission spectrum of the QD-LED device to study the exciton distribution. Organic phosphorescent molecule, Ir(III)(phq)₂(acac) is placed in the TCTA layer to harvest all of the excitons in the TCTA layer. This emission spectrum was recorded at 22.22 mA cm⁻². The device corresponding energy band diagram for this study is shown in the inset. Reprinted with permission from Reference [110]. Copyright 2013 American Chemical Society.

We then studied the exciton distribution of the QD device to understand the factors that cause the performance improvement. The studied device consisted of ITO (150 nm)/PEDOT:PSS (60 nm)/poly-TPD (30 nm)/QD active layer (20 nm)/TCTA: Bis(2-phenylquinoline)(acetylacetonate)iridium(III) (Ir(III)(phq)₂(acac)) (5%, 20 nm)/TPBi (35 nm)/LiF (0.5 nm)/Al (150 nm). The Ir(III)(phq)₂(acac) is a highly efficient phosphorescent organic molecule which can harvest all excitons formed in the TCTA layer to emit orange-red light. The emission spectrum of the studied device with the Ir(III)(phq)₂(acac) doped TCTA layer at 22.22 mA cm⁻² is shown in Figure 5-8. This emission spectrum consists of green QD and Ir(III)(phq)₂(acac) molecule emission with their emission peak located at 512 and 596 nm, respectively. Here we deconvoluted QD and Ir(III)(phq)₂(acac) emissions by curve fitting method to determine the fraction of light emission, as shown in Figure 5-9.

From Figure 5-9 we observed that the QD component is the main contributor in the emission. The exciton formed in the QD and TCTA layers can then be calculated using the following:

$$Exciton_{QD\ layer} = \frac{\int I_{QD}(\lambda)d\lambda/EQE_{QD}}{\int I_{QD}(\lambda)d\lambda/EQE_{QD} + \int I_{sensing}(\lambda)d\lambda/EQE_{sensing}} \quad (5.1)$$

$$Exciton_{sensing\ layer} = \frac{\int I_{sensing}(\lambda)d\lambda/EQE_{sensing}}{\int I_{QD}(\lambda)d\lambda/EQE_{QD} + \int I_{sensing}(\lambda)d\lambda/EQE_{sensing}} \quad (5.2)$$

where exciton_{QDlayer} and exciton_{sensinglayer} denote the excitons located in the QD and TCTA layers, respectively; I_{QD} and I_{sensing} are the respective measured

intensity of QD or Ir(III)(phq)₂(acac) emission at the given wavelength. EQE_{QD} is the maximum EQE obtained from our QD-only device (without a sensing layer, we used EQE_{QD} = 3.14%), and EQE_{sensing} is the maximum EQE obtained using ITO (150 nm)/PEDOT:PSS (60 nm)/poly-TPD (30 nm)/TCTA: Ir(III)(phq)₂(acac) (5%, 20 nm)/TPBi (35 nm)/LiF (0.5 nm)/Al (150 nm) device structure (where we used EQE_{sensing} = 20%).

Figure 5-9: Curve-fitting of the QD-LED device electroluminescence to study the exciton distribution using QD and Ir(III)(phq)₂(acac) components.

The deconvolution study shows that 97% of the exciton formation takes place in the QD layer, while only 3% of the excitons formed in the TCTA layer. Due to the limited exciton formation outside QD layer, the energy transfer from the organic transport layer to QDs is found to be miniscule. The device

enhancement in EQE is mainly due to the charge balance improvement in the system. We then used the same principle to fabricate hybrid devices with different size QDs. The devices with QDs sandwiched between the HTLs consistently showed EQE improvement. Here we achieved four times improvement in EQE for the blue-emitting device, and fivefold EQE improvement in the green- and red-emitting devices.

Organic small molecules are very sensitive to the oxygen and moisture in the surrounding environment. Although the performance of the proposed devices improved significantly compared to the reference device, the additional organic layer may pose some operational stability issues, for example, faster degradation. To address this concern we carried out the lifetime measurement for the devices. The device structures used in the lifetime study consist of ITO (150 nm)/PEDOT:PSS (60 nm)/poly-TPD (30 nm)/QD emissive layer (20 nm)/TCTA (0 or 20 nm)/TPBi (35 nm)/LiF (0.5 nm)/Al (150 nm). Figure 5-10 shows the operating lifetime measurement data for the devices with and without TCTA. The luminance of the devices was measured with continuously applying a constant current density to the devices. The initial luminance of these devices is 1000 cd m^{-2} . Both QD-LED devices were fabricated using the same QDs and characterized at the same ambient temperature and level of humidity with no device encapsulation. Figure 5-10 clearly shows that the operating lifetime of the proposed device (with TCTA) is comparable to the reference device (without TCTA), implying that additional TCTA layer does not reduce the operating lifetime of the device.

Figure 5-10: Operational lifetime characteristics of the QD-LEDs with and without additional TCTA HTL.

5.4 Conclusion

In summary, we demonstrated high-efficiency hybrid organic/inorganic QD-LEDs using a new device architecture in which the QD emissive layer is sandwiched inside the HTL. More than five-fold luminance and EQE enhancements are achieved as compared to the reference structure. These improvements come from the better exciton confinement in the QDs and the balance of charge carrier injection into the QDs active layer. The nonradiative energy transfer between the organic layer and QDs in this device structure is found to be miniscule. The results open up a simple and efficient pathway to

manufacture high performance QD-based optoelectronic devices by placing the QDs active layer inside the hole transporting layers.

CHAPTER 6: Efficient Interface Modification in Hybrid Organic/Inorganic Quantum Dot-Light Emitting Diodes using Low Workfunction Materials

In this chapter, we studied the effect of electron injection layer (EIL) on the performance of the non-inverted all-organic charge transport layer based quantum dot light-emitting device (QD-LED). The incorporation of cesium carbonate (Cs_2CO_3) into the QD-LEDs as EIL could improve the electron injection and reduce the device operating voltage, resulting in the QD-LED's performance enhancement. The use of Cs_2CO_3 as EIL has reduced the operation voltage by 19%, while the external quantum efficiency (EQE) and the power conversion efficiency have been improved by 35% and 24%, respectively, compared to the reference device, which uses lithium fluoride (LiF) as the EIL. In the first part of the chapter a brief introduction and the objective of this study are provided, followed by a series of experiments and findings. Results are discussed in the third part of the chapter and conclusion of this chapter is given in the last part.

6.1 Introduction

Since the first electroluminescent QD-LED demonstrated by Alivisato's group two decades ago [4], a lot of efforts have made to improve the device performance towards high brightness and external quantum efficiency (EQE) steadily, thanks to the advanced technological research and development over years, such as improving device architecture design, the availability of superior charge transport layers, optimizing quantum dot properties and stability, and most importantly, the better understanding of the QD device physics [6, 8, 45, 55, 57, 66, 97, 121, 127]. It is widely agreed that QD devices are very sensitive to the interfaces between adjacent layers [58, 128, 129]. These interfaces depend on the physical morphology of the films and the energy band barrier between the two adjacent layers, for examples, the difference on energy levels introduced by the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of two layers. The interfaces determine the hole and electron injection rate, the device operating voltage and the exciton formation zone. Any favourable carrier injection could alter the exciton formation zone and affect the charge balance at the emissive layer, which therefore affects the device performance. Therefore, interface engineering must be handled properly in order to achieve high efficient QD-LEDs.

In this chapter, we demonstrate an improved QD-LED with double-sided organic CTL architecture using Cs_2CO_3 as the electron injection layer (EIL). The proposed device that employs Cs_2CO_3 EIL shows 35% increase in EQE, a 19% reduction in operating voltage and a 24% improvement in power

conversion efficiency compared to the reference device that uses LiF as EIL. In addition to the operating voltage reduction here, it is discovered that the improvement is also coming from the reduction of excitons that leak into the additional adjacent HTL in the electron injection side. The best green device reaches an EQE level of 4.24%, and power conversion efficiency up to 5.49 lm/W. To the best of our knowledge it is the highest reported value for the QD-LED device architecture with double-sided organic CTLs.

6.2 Experimental Session

6.2.1 QD Synthesis and Purification

Green-emitting alloyed CdZnSeS quantum dots ($\lambda_{\text{peak}} = 506 \text{ nm}$) with a composition gradient were synthesized based on the protocols reported in the literature [6, 110] as follows: cadmium oxide (CdO, 0.1 mmol) and zinc acetate dihydrate ($\text{Zn}(\text{Acet})_2 \cdot 2 \text{ H}_2\text{O}$, 4 mmol), oleic acid (OA, 5 mL) and 1-octadecene (1-ODE, 15 mL) was added into a 100 mL three-neck flask and heated for 30 min at 100 °C in vacuum environment. The flask was then filled with nitrogen gas to 1 atm and the temperature was increased to 300 °C. Once the solution reached 300 °C, 2 mL of tri-octylphosphine (TOP) stock solution containing selenium (Se, 0.15 mmol) and sulphur (S, 4 mmol) were quickly added into the solution mixture and the solution temperature was kept at 300 °C for 10 min to complete alloyed CdZnSeS nanocrystals growth.

The excess ligand and unreacted materials in the QD crude solution were removed by standard precipitation/redispersion process as discussed in chapter 3. Finally, the purified QDs were redispersed using fresh toluene with a concentration of 15 mg mL^{-1} for further use. The QDs exhibited a QY of 60% in toluene by comparing the fluorescence intensity with fluorescein-27 standard dye in 0.1 M NaOH solution [105]. The QY of the QD film was characterized to be 40% using the absolute photoluminescence (PL) QY measurement system (Hamamatsu Quantaurus-QY).

6.2.2 Device Fabrication

The patterned-ITO glass substrate with a sheet resistance of $25 \Omega/\square$ was first cleaned with a routine procedure including consecutive ultrasonication in Decon 90 detergent, Milli-Q Millipore de-ionized (DI) water, acetone and isopropanol, and dried in oven at 80°C overnight. Before fabrication, 10 min of O_2 plasma was applied to the substrates to improve the ITO surface wettability. PEDOT:PSS was first spin-coated at the speed of 3000 rpm and baked for 30 min in N_2 atmosphere, followed by hole transport layer (poly-TPD) and active layer (QDs). On top of that, another hole transport layer, 4,4',4''-tris-(carbazol-9-yl) triphenylamine (TCTA), electron transport layer (1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene, TPBi), electron injection layer (Cs_2CO_3 , LiF or Ca) and metal cathode (aluminium, Al) were thermally deposited. The deposition speed of organic materials were maintained at $1 \text{ \AA s}^{-1}$, while the deposition rate of EIL and metal cathode were $0.1 \text{ \AA s}^{-1}$ and $3 \text{ \AA s}^{-1}$,

respectively. The thickness of the organic layer was monitored in situ by calibrated quartz crystal microbalance and the device active layer is defined to be 9 nm².

6.2.3 Device Measurement

Measurement of QD-LEDs luminance and emission spectra were performed using a LabView-controlled Konica-Minolta LS-100 luminance meter and PhotoResearch SpectraScan PR705 spectroradiometer, respectively, while the electrical characterization was measured using a Yokakawa GS610 source measurement unit. Details of measurement and calculation were described in chapter 3.

6.3 Results and Discussions

The device structure of the studied QD-LEDs and their energy band diagrams are shown in Figure 6-1. The structure of the QD-LEDs with the organic ETL [110] fabricated in this study consists of tin-doped indium oxide (ITO, 150 nm)/PEDOT:PSS (60 nm)/poly-TPD (30 nm)/QD emissive layer (20 nm)/TCTA (20 nm)/TPBi (35 nm)/lithium fluoride (LiF, 0.5 nm)/aluminum (Al, 150 nm). Here the PEDOT:PSS serves as a hole injection layer (HIL) to facilitate the hole injection, whereas poly-TPD serves as a hole transport layer (HTL), TPBi and LiF are used as ETL and EIL, respectively. Our previous works addressed the charge imbalance issue and showed that the addition of a

20 nm thick TCTA between the QD and TPBi improved the device performance up by 5-folds compared to the device without any TCTA layer. Such improvement is mainly due to the charge balance improvement in the QD emissive layer [110]. However, the low conductivity of the organic materials had caused the device's operating voltage comparatively to be higher than those devices using inorganic charge transport layers and this unavoidably lowers the power conversion efficiency. In order to reduce the device operating voltage, we adapt a similar method from organic LED (OLED) research by introducing alkali/alkaline metal complex at the ETL/cathode interface to improve the charge injection [130-134]. Alkali/alkaline metal complexes have a low workfunction that can be used to reduce the energy difference between the cathode and organic transport layer and hence to improve the charge injection. In this chapter, QD-LEDs are characterized by changing the EIL with caesium carbonate (Cs_2CO_3), lithium fluoride (LiF) and calcium (Ca) which have different workfunctions to study the effect on the device performances. These three electron injection materials are widely used in the OLED devices to minimize the barrier between the organic materials and electrode to reduce the operating voltage [55, 130, 131, 135, 136].

Figure 6-1: (left) Device structure and (right) band diagram of the studied QD-LEDs.

Figure 6-2: Current density-voltage (J-V) characteristics of the studied QD-LEDs using different EILs.

Figure 6-2 shows the effects of using different electron injection layers (LiF, Cs₂CO₃, and Ca) in the QD-LEDs and their current density-voltage (J-V) characteristics are shown in Figure 6-2. This shows that, the use of EIL in the

device architecture lead to a remarkable improvement in current compared to the device without EIL, indicating the EIL effectively reduces the energy gap between TPBi ETL and Al cathode. At a current density of 1 mA cm^{-2} , the operating voltage of the Cs_2CO_3 -based device is 5.78 V, whereas the devices using LiF and Ca as the EIL have operating voltages of 6.20 V and 9.20 V, respectively. In comparison, the operating voltage of the device without any EIL is 12.80 V.

Figure 6-3: Luminance-voltage (L-V) curve of the quantum dots light-emitting devices using different electron injection layers.

From the luminance-voltage characteristics presented in Figure 6-3, we also found that the luminance of the devices is improved significantly with the addition of EILs. The operating voltages of the devices using Cs_2CO_3 , LiF, and

Ca as the EIL at a brightness level of 100 cd m^{-2} are 7.60, 9.40, and 11.00 V, respectively, compared to 13.40 V of the device without using EIL. The J-V and L-V characteristics shown in Figure 6-2 and 6-3 clearly indicate that the devices using Cs_2CO_3 as EIL can achieve better performance than using other EIL materials. Cs_2CO_3 has a lower workfunction (-1.9 eV) than LiF (-2.5 eV), Ca (-2.9 eV) and Al cathode (-4.08 eV) [135, 137, 138], and therefore it has a better ability to reduce the energy barrier between the ETL and cathode. In addition, Huang *et al.* showed that Cs_2CO_3 behaves as a heavily n-doped semiconductor that connects Al cathode and TPBi EIL [135]. Electrons can be injected into the device at a minimum voltage drop and recombine with the holes that are injected from PEDOT:PSS to generate photons.

Figure 6-4: Current density-luminance-voltage (J-L-V) characteristics of the QD-LEDs with different film thicknesses of Cs_2CO_3 injection layers.

We also characterized the QD-LEDs with different film thicknesses of Cs_2CO_3 (0 to 2.4 nm) to further study the effect of Cs_2CO_3 on the device performance and their corresponding current density-luminance-voltage (J-L-V) characteristics are shown in Figure 6-5. The presence of the Cs_2CO_3 EIL results in a large change in the current density and luminance curves. We observed a notable enhancement in the current injection and luminance even we use a very thin (0.6 nm) Cs_2CO_3 layer. For the thicknesses used in this study, a thicker Cs_2CO_3 film can facilitate electron injection.

Figure 6-5: EQE-current density characteristics of the QD-LEDs with different thickness of Cs_2CO_3 injection layers. Inset showed the enhancement factor of EQE using different Cs_2CO_3 thicknesses.

Figure 6-5 shows the EQE versus current density characteristics of the devices given in Figure 6-4 and the inset shows the enhancement factor with respect to the device without Cs_2CO_3 EIL at a current density of 10 mA cm^{-2} . The highest EQE, current efficiency and power conversion efficiency achieved in the device using a 1.2 nm thick Cs_2CO_3 are 4.24%, 10.25 cd A^{-1} , and 5.49 lm W^{-1} , which represents large improvement compared to the value of 3.14%, 8.7 cd A^{-1} and 4.4 lm W^{-1} obtained from the highest device performance using LiF as EIL to date [110]. The device without EIL exhibits limited performance in maximum EQE of 2.69%, current efficiency of 6.47 cd A^{-1} , and power conversion efficiency of 1.34 lm W^{-1} .

Figure 6-6: Electroluminescence spectra of the QD-LEDs utilizing LiF and Cs_2CO_3 electron injection layer. The TCTA layer is doped with Ir(III)(phq)₂(acac) red phosphorescent materials to study the exciton distribution.

Deposition of low workfunction inorganic electron injection materials between the organic ETL and metal cathode not only reduces the band barrier between the two layers but also causes doping effect in the organic layer [130, 132-134]. This could cause the exciton formation zone to be shifted toward the emissive QD layer, resulting in EQE enhancement. To rationalize this observation, we studied the exciton distribution in the devices by doping TCTA layer with an efficient red phosphorescent organic material, Bis(2-phenylquinoline)(acetylacetonate)iridium(III) ($\text{Ir(III)(phq)}_2(\text{acac})$). The devices structure in this study was ITO (150 nm)/PEDOT:PSS (60 nm)/poly-TPD (30 nm)/QD active layer (20 nm)/TCTA (10 nm)/TCTA: $\text{Ir(III)(phq)}_2(\text{acac})$ (95%: 5%, 10 nm)/TPBi (35 nm)/EIL (LiF or Cs_2CO_3 , 0.5 nm)/Al (150 nm). Figure 6-7 shows the normalized electroluminescence spectra of the studied devices. The electroluminescence spectra were recorded under current density of 10 mA cm^{-2} . The emission spectra come from the combination of the QD (emission peak at 512 nm) and $\text{Ir(III)(phq)}_2(\text{acac})$ (emission peak at 596 nm) components. For both devices, excitons are formed either inside the QD emissive layer or at the TCTA/TPBi interface. Deconvolution study [139] predicts that for the device with EIL of LiF, 5% of the excitons leak into the TCTA/TPBi interface, whereas only 3% of the excitons leak to the TCTA/TPBi interface for the device with EIL of Cs_2CO_3 . The Cs_2CO_3 ETL reduces the exciton leakage and more excitons are confined in the QD emissive layer and contribute to the radiative decay, resulting in EQE improvement.

6.4 Conclusion

In summary, we studied the effect of electron injection materials on the QD-LEDs using double-sided organic CTLs. Significant improvement is obtained by the insertion of low workfunction Cs_2CO_3 material as EIL. The reduction of charge barrier between the electron transport layer and cathode, and the reduction of exciton leakage to the organic layer leads to the performance improvement. The results provide important guidance for designing and fabricating high-performance QD-based optoelectronic devices.

CHAPTER 7: Gallium-doped Zinc Oxide (GZO) as Tin-doped Indium Oxide (ITO) Alternative For Transparent Electrode in QD-LEDs

To date, tin-doped indium oxide, also abbreviated as indium tin oxide (ITO), is widely used in optoelectronic devices as the transparent conducting electrode. Due to the scarcity of indium source, the price of the ITO increases annually, resulting in the increased fabricating and manufacturing cost. In this chapter, we demonstrate colloidal quantum dot light-emitting diodes (QD-LEDs) using abundant gallium-doped zinc oxide (GZO) as a transparent conducting anode and achieve device performance comparable to the device using ITO. We first provide background and objectives of this study, followed by the details of systematic experiments. The experimental results and discussions are discussed in the third part of this chapter and the conclusion is given in the last part.

7.1 Introduction

QD-LEDs have been attracting a lot of attention owing to their potential for providing highly-efficient, low-cost devices [62, 67, 117, 118]. Since the first QD-LED demonstrated in 1994 [4], most of the research works have

utilized ITO as QD device's transparent conducting oxide (TCO) [6, 8, 43, 54, 110, 123, 140-142] for electrodes. Over the past four decades, ITO has become the most commonly used TCO in the institutional research and commercial optoelectronic applications including light-emitting devices, photovoltaics, photodetectors, and flat-panel displays, thanks to their attractive properties such as high conductivity ($\sim 10^3 \text{ S cm}^{-1}$) and high transparency of up to 90% (at the optical wavelength of 550 nm). Due to large demand, the consumption of ITO increases annually. Combined with the limited availability of indium source, it is foreseeable to be a problematic issue that the price of ITO will keep rising and thus the fabrication cost will increase [36, 143]. Therefore, finding an alternative TCO which has similar optical and electrical performance as ITO, is essential. A lot of effort has been made to develop ITO alternatives that are relatively low-cost and high-performance (transparency and conductivity) comparable to the ITO [144-146].

Zinc oxide (ZnO) doped with group (III) elements (e.g., aluminum, gallium) has been longtime suggested to be a good TCO to serve as an electrode in organic light-emitting diodes. The high transparency, conductivity, stability and the wide optical bandgap energy ($>3 \text{ eV}$) of ZnO allow it to be implemented in optoelectronic applications in the visible and the near-ultraviolet window [143]. GZO has been thought as a suitable transparent electrode material to replace ITO. In this chapter we demonstrate QD-LEDs using GZO as a transparent electrode. The fabricated GZO film has a resistivity and sheet resistance of $9.48 \times 10^{-4} \text{ } \Omega \cdot \text{cm}$ and $12.28 \text{ } \Omega/\square$, respectively, which are

close to the commercial grade ITO performance. We then utilize the GZO film for device fabrication and achieve a device performance level close to the device using an ITO electrode, showing the potentials of GZO as an ITO alternative as a transparent conducting electrode.

7.2 Experimental Details

7.2.1 GZO Film Deposition

Transparent conducting GZO films were deposited on soda lime glass substrate using Oerlikon Leybold UNIVEX 350 RF magnetron sputtering system with a 3-inch $\text{Zn}_{0.95}\text{GaO}_{0.05}$ target (purity 99.99%, Super Conductor Materials Inc). Prior to thin film deposition, the glass substrates were cleaned routinely in ultrasonic bath using detergent (Decon 90), de-ionized (DI, Milli-Q millipore) water, acetone and ethanol, followed by drying them in oven at 80 °C for 30 min before loading into the deposition chamber. All deposition was started at the base pressure of 5×10^{-6} mTorr. For a typical deposition process, GZO thin films were performed in a mixed argon/oxygen environment (40:1) and the deposition rate was maintained at 10 nm per minute. After deposition, they were further annealed at a temperature of 600 °C for 2 h in vacuum environment to enhance the film conductivity and transparency.

Transmittance spectra of the GZO films were recorded using Shimadzu Spectrophotometer UV-1800, while their sheet resistance was evaluated using a

4-point probe technique (Advanced Instrument Technology CMT-SR2000T). The film thickness and crystallinity of the GZO film were evaluated using a Dektak 150 surface profiler and a Siemens x-ray diffraction spectroscopy (XRD), respectively.

7.2.2 QD Synthesis and Purification

Green-emitting alloyed CdZnSeS quantum dots ($\lambda_{\text{peak}} = 506 \text{ nm}$) with a composition gradient were synthesized using the following modified protocol as follows [6, 110]: cadmium oxide (CdO, 0.1 mmol), zinc acetate dihydrate ($\text{Zn}(\text{Acet})_2 \cdot 2 \text{ H}_2\text{O}$, 4 mmol), and oleic acid (OA, 5 mL) were added into a 100 mL 3-neck flask and heated up to 150 °C for cadmium oleate ($\text{Cd}(\text{OA})_2$) and zinc oleate ($\text{Zn}(\text{OA})_2$) formation. After that, the solution was added 1-octadecene (1-ODE, 15 mL), which served as a non-coordinating solvent and the solution temperature was reduced to 100 °C and maintained under vacuum environment for 30 min. After that, the flask was filled with nitrogen gas and the temperature was increased to 300 °C. 2 mL of TOP:Se and TOP:S solution was injected into the flask and the solution temperature was regulated at 300 °C for alloyed CdZnSeS nanocrystal growth. The synthesis took 10 min to complete.

The excess ligand and unreacted materials in the QD crude solution were removed by standard precipitation/redispersion process as discussed in chapter 3. Finally, the purified QDs were redispersed into toluene with a

concentration 10 mg/mL for further uses. The QDs' quantum yield (QY) was measured to be 75% using the absolute QY measurement technique.

7.2.3 Synthesis of Zinc Oxide (ZnO) Nanoparticles

ZnO nanoparticles were synthesized based on the reported protocol [66] as follows: zinc acetate dihydrate ($\text{Zn}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$, 3 mmol) was first dissolved in 30 mL of dimethyl sulfoxide (DMSO) and the Zn-contained stock solution was stirred vigorously for 10 minutes. After that, 10 mL of ethanol contained 5 mmol of tetramethylammonium hydroxide (TMAH) was added dropwise into the Zn-stock solution. The reaction solution was stirred for 1 h in the room temperature for the formation of ZnO nanoparticles.

The ZnO nanoparticles were extracted by adding excess acetone followed by 5000 rpm centrifugation for 5 minutes. The supernatant was removed and the white ZnO precipitate at the bottom of the centrifugal tube was collected and dried in vacuum environment, and redispersed into ethanol with a concentration of 20 mg mL^{-1} . A transmission electron micrograph (TEM) image of the ZnO nanoparticles is shown in Figure 7-1. The size of the ZnO nanoparticles is 4-5 nm.

Figure 7-1: Transmission electron micrograph (TEM) of ZnO nanoparticles. The nanoparticles have a size of 4-5 nm.

7.2.4 QD-LED Fabrication

Prior to the device fabrication, glass substrates coated with GZO film were patterned and sonicated in detergent for 30 min. The cleaning procedure was repeated thrice and each with different solvents (de-ionized (DI) water, acetone, and isopropyl alcohol (IPA)) before drying inside the oven at 80 °C overnight. 10 minute O₂ plasma treatment was applied to the substrates to improve the surface wettability before loading into the glovebox for device fabrication.

Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) was first spin-coated at 3000 rpm in N₂ environment and anneal for 30 minutes. After that, poly-TPD (hole transport layer) and QDs (emissive

layer) were deposited subsequently. On top of that, ZnO nanoparticle, which served as electron transport layer, was spin-coated at 2000 rpm and baked for 30 minutes, and finally 150 nm of Al were deposited using thermal deposition technique. The Al deposition rate was maintained at $3 \text{ \AA s}^{-1}$ to ensure the film uniformity. The effective area of the LED devices is 9 mm^2 .

7.2.5 QD-LED Measurement

Measurement of QD-LEDs luminance and emission spectra were performed using a LabView-controlled Konica-Minolta LS-100 luminance meter and PhotoResearch SpectraScan PR705 spectroradiometer, respectively, while the electrical characterization was measured using a Yokakawa GS610 source measurement unit. Details of measurement and calculation were described in chapter 3.

7.3 Result and Discussion

Table 7-1 summaries the sheet resistance and the resistivity of the as-grown GZO films and the GZO after performing post-annealing process at 600°C . The GZO film thickness was varied from 180 to 772 nm. It is clear that the as-grown GZO films have a rather high sheet resistance and resistivity. The 180 nm thick GZO film has a sheet resistance and resistivity of $309.9 \text{ }\Omega/\square$ and $5.58 \times 10^{-3} \text{ }\Omega \cdot \text{cm}$ respectively, and both of them reduce gradually when the film thickness increases. The post-annealing process at 600°C in vacuum

environment efficiently decreases the resistivity of the GZO films. The lowest sheet resistance and resistivity are $12.28 \Omega/\square$ and $9.48 \times 10^{-4} \Omega \cdot \text{cm}$, respectively, which were obtained from the 772 nm thick GZO film. We attributed the low resistivity of the high thickness of GZO films to the post annealing process. The electrical performance of the GZO is comparable to the commercially available ITO glass substrate ($15 \Omega/\square$).

Table 7-1: Sheet resistance of the as-grown and annealed GZO films.

Deposition time	Film thickness	R_s (as grown)	ρ (as grown)	R_s (post annealed)	ρ (post-annealed)
30 min	180 nm	$309.90 \Omega/\square$	$5.58 \times 10^{-3} \Omega \cdot \text{cm}$	$178.10 \Omega/\square$	$3.21 \times 10^{-3} \Omega \cdot \text{cm}$
60 min	360 nm	$143.84 \Omega/\square$	$5.18 \times 10^{-3} \Omega \cdot \text{cm}$	$44.06 \Omega/\square$	$1.59 \times 10^{-3} \Omega \cdot \text{cm}$
90 min	530 nm	$92.17 \Omega/\square$	$4.89 \times 10^{-3} \Omega \cdot \text{cm}$	$24.81 \Omega/\square$	$1.32 \times 10^{-3} \Omega \cdot \text{cm}$
120 min	772 nm	$30.52 \Omega/\square$	$2.36 \times 10^{-3} \Omega \cdot \text{cm}$	$12.28 \Omega/\square$	$9.48 \times 10^{-4} \Omega \cdot \text{cm}$

High temperature post-annealing process can improve the crystallinity of the GZO films, leading to increased carrier concentration and mobility, which can reduce the sheet resistance. To confirm this finding, x-ray diffraction (XRD) analysis was performed. The XRD spectra of the GZO films are shown in Figure 7-2. We observed a sharp (0002) peak at $2\theta = 34.14^\circ$ on the GZO films after post-annealing. This indicates that the annealed GZO films show a good c-axis orientation, i.e. perpendicular to the glass substrate. Good film crystallinity can enhance the carrier concentration and mobility that can effectively reduce the film resistivity. The increased carrier concentration is

caused by the substitution of Ga^{3+} ions into the Zn sites in the ZnO lattice at high temperatures [147].

Figure 7-2: X-ray diffraction spectra of the GZO films after annealing process.

For a good TCO candidate, the absorbance of the film should be as low as possible in the effective range of wavelength, i.e. should have high transmission in visible spectrum. We then studied the effects of the GZO film thickness on the light transmission. The transmission spectra were obtained and plotted in Figure 7-3. The transmittance of the GZO films is more than 80% in the entire visible window and no significant difference in the optical absorption were observed with film thickness variation in this range. In comparison,

transmittance of the commercial grade ITO shows 20% reduction in light transmission when the thickness is doubled to 240 nm.

Figure 7-3: Transmission spectra of the GZO films and commercially available ITO films at different film thickness in visible spectrum window.

The optical energy bandgap (E_g) of the GZO film is determined using the method proposed by Park *et al.* based on the transmittance spectrum of GZO film [147]. From Beer-Lambert Law, the transmittance equation is of a GZO film is defined as

$$T = \frac{I}{I_0} = e^{-\alpha t} \quad (7.1)$$

where T is the transmittance of the GZO film, I is the transmitted light intensity after passing through the GZO film, I_0 is the incident light intensity, α and t are the optical absorption coefficient and the thickness of the GZO film, respectively. In addition, α and the optical bandgap E_g can be related in the following equation,

$$\alpha = \left(\frac{hc}{\lambda} - E_g\right)^{\frac{1}{2}} \quad (7.2)$$

where h is the Planck's constant, c is the velocity of light in vacuum environment, and λ is the wavelength of the incident light. The first term, hc/λ , denotes the incident photon energy. Taking square at both sides of Equation 7.2, we arrive

$$\alpha^2 = \frac{hc}{\lambda} - E_g \quad (7.3)$$

The square of optical absorption coefficient as a function of incident photon energy (α^2 vs hc/λ) is presented in Figure 7-4. It is observed that with photon energy greater than the bandgap, α^2 and hc/λ showed linear dependency, which implies that the deposited GZO film is direct bandgap semiconductor. Due to the linearity, when α^2 is zero, we can obtain the optical bandgap E_g . By applying extrapolation method in the linear region of the curves, we found that E_g of the GZO film is 3.40 ± 0.10 eV, which fulfills the requirement of TCO that the optical bandgap of the candidate should be >3 eV.

Considering its low resistivity, high transmittance and wide optical bandgap properties, we can utilize the GZO film in QD-LEDs as a transparent electrode.

Figure 7-4: Square of optical absorption coefficient as a function of incident photon energy.

We also determined the effective workfunction of the GZO film using the ultraviolet photoelectron spectroscopy (UPS). The corresponding UPS spectrum is given in Figure 7-5. The excitation source was chosen to be He(I) source, which has a photon energy of 21.2 eV. The workfunction (ϕ_{WF}) of the GZO film is characterized by the difference between the source energy and photoemission spectrum width, as shown in Equation 7.4:

$$\phi_{WF} = h\nu - \Delta E = 21.2 \text{ (eV)} - \Delta E \quad (7.4)$$

where ΔE is the energy difference between the ionization energy and the photoemission cut-off of the UPS spectrum.

From Figure 7-5, the photoemission onset is found at 19.79 eV and the ionization energy of the GZO film is determined to be 3.04 eV with respect to the Fermi level. We therefore obtained the workfunction of GZO to be 4.45 eV, which is in agreement with the workfunction value reported in the literature, ranging from 4.1 to 4.6 eV depending on the method of film preparation [143, 145, 146, 148].

Figure 7-5: UPS spectrum of the GZO film. The dotted line shows the photoemission onset and ionization energy of the GZO film.

A series of QD devices were fabricated to evaluate the suitability of GZO film as TCO for QD-LEDs. A device using ITO as anode was also fabricated and served as the reference device for comparison. The device structures of the QD-LEDs are:

- a) ITO (120 nm)/PEDOT:PSS (60 nm)/poly-TPD (30 nm)/QD (20 nm)/ZnO (50 nm)/Al (150 nm)
- b) GZO (180 nm)/PEDOT:PSS (60 nm)/poly-TPD (30 nm)/QD (20 nm)/ZnO (50 nm)/Al (150 nm)
- c) GZO (360 nm)/PEDOT:PSS (60 nm)/poly-TPD (30 nm)/QD (20 nm)/ZnO (50 nm)/Al (150 nm)
- d) GZO (540 nm)/PEDOT:PSS (60 nm)/poly-TPD (30 nm)/QD (20 nm)/ZnO (50 nm)/Al (150 nm)

Figure 7-6: (left) Device structure and (right) band diagram of the studied non-inverted QD-LEDs using GZO/ ITO as the anode.

The device schematic and their corresponding energy band diagram are shown in Figure 7-6. In this structure, both ITO and GZO serve as the device anode, while PEDOT:PSS serves as the hole injection layer (HIL) and poly-TPD as the hole transport layer (HTL). QD layer is placed at the interface to convert electron hole pairs into photons. ZnO nanoparticles function as the electron transport layer (ETL) and Al as the cathode. The 772 nm thick GZO film was not employed in the device fabrication due to their large step size between the film and glass substrate. In this case, the spin-coated film (PEDOT:PSS, poly-TPD, QD, ZnO) was not uniform and caused device to short-circuit.

Figure 7-7 shows the current density-voltage (J-V) characteristics of the devices using various thicknesses of GZO as the anode. Under the same operating voltage of 10 V, the measured current density of the 180 nm, 360 nm and 540 nm thick GZO devices are 106.68, 193.13 and 306.30 mA cm⁻², respectively. It is clear that the current density increases with the GZO film thickness. When the thickness of GZO film increases, the sheet resistance of the anode reduces and the carriers can be easily injected into the device, resulting in higher current density under the same operating voltage. In comparison, the reference device utilizing commercially available ITO has the lowest sheet resistance compared to that of GZO films (15 Ω/□ versus 178, 44, and 24 Ω/□, respectively). Therefore it has the highest current density of 365.65 mA/cm².

The luminance versus voltage (L-V) characteristics is shown in Figure 7-8. All 4 devices obtained a luminance level exceeding 1000 cd m^{-2} , which is suitable for the general lighting purposes. The turn-on voltages of the QD-LEDs are 3.35, 3.08 and 3.01 V, respectively, for the devices using 180, 360, and 540 nm thick GZO anodes, compared to the ITO device with a turn-on voltage at 3.42 V. Here the turn-on voltage is the operating voltage to achieve luminance of 1 cd m^{-2} .

Figure 7-7: Current density - voltage (J-V) characteristics of the studied devices.

Figure 7-8: Luminance - voltage (L-V) characteristics of the QD-LED devices using different thicknesses of GZO and ITO anode.

The external quantum efficiency (EQE) versus current density is given in Figure 7-9. It is clear that devices using GZO as the anode have a similar performance to ITO device. At the current density of 100 mA cm^{-2} , the EQE of the devices using 180, 360, and 530 nm thick GZO anodes are 0.52%, 0.99%, and 1.13%, respectively, comparing to the 1.07% EQE which was obtained from the ITO device, showing the capability of GZO film as the ITO alternative for the TCO. It is worth noting that the device efficiency can be further improved by optimizing the thickness and the structure of the transport layer and the injection layer.

Figure 7-9: EQE-current density characteristics of the studied devices.

7.4 Conclusion

In conclusion, we have successfully deposited conducting and transparent GZO films on glass substrates using RF sputtering technique as a viable alternative to ITO electrodes for the QD-LEDs. The sheet resistance and resistivity reduce gradually with respect to the film thickness with thermal annealing. With post annealing process, the resistivity can be as low as the commercially available ITO. Moreover, the QD-LEDs fabricated on the GZO electrodes show a similar performance level to those prepared on the ITO electrode. This shows that the indium-free ZnO-based transparent conducting electrode fabricated by sputtering process is a promising anode material for

low-cost QD-LEDs, owing to its high conductance and optical transmittance,
low-temperature process, and low cost.

CHAPTER 8: Conclusion and Future Work

8.1 Conclusion

In this thesis, our research focusses on colloidal quantum dot light-emitting diodes (QD-LEDs) targeting improved device performance. We first demonstrated white colloidal quantum dot light-emitting diodes with emission spectrum covering entire visible spectrum window. The realization of white emission was achieved using a specially designed loosely packed QD layer in which the electron and hole transport layers (TPBi and poly-TPD, respectively) are partially in contact. Certain amount of the injected electrons and holes were allowed to bypass the QD layer and recombined in the transport layers. White emission consisted of blue, green and red emission from the poly-TPD, green-emitting QDs, and exciplex originated from the interface recombination between poly-TPD and TPBi, respectively. The fabricated QD-LEDs showed high colour rendering index (CRI) of 89, which is very promising for the practical usage in quality lighting applications.

Secondly, we showed that the efficiency of hybrid QD-LEDs can be improved by sandwiching the QD emissive layer inside the hole transporting layers (poly-TPD and TCTA). With this proposed device structure, the performance exhibit more than fivefold improvement compared to the reference device in which the QD layer is placed at the interface of hole and electron transport layers. Systematic analysis revealed that the resulting improvement is

mainly due to the balanced charge carrier injection into the QDs active layer and better exciton confinement in the QD layer. Exciton distribution of the QD-LEDs was studied and it was found that energy transfer between the large bandgap organic materials and QDs in this architecture is minimal as majority of the excitons were formed in QD layer. The proposed device architecture with active QDs placed inside hole transporting layers in this work offers a simple, yet efficient pathway to improve the device performance.

Although significant improvement of device performance has been possible with the insertion of additional TCTA HTL between the QD layer and ETL, we also observed that the interface could be further optimized. It is possible to adapt similar strategies widely used for the organic LEDs, e.g., by changing larger workfunction lithium fluoride (LiF) to other low workfunction surface modification materials, such as cesium carbonate (Cs_2CO_3). In the thesis, the effect of electron injection materials to the QD-LED device performance was studied and notable performance improvement was obtained from the Cs_2CO_3 electron injection layer (EIL). The improvement is mainly due to the surface modification between electron transport layer and cathode, where energy barrier between the two layers was reduced effectively. From the device exciton distribution, it was found that the use of Cs_2CO_3 enables better exciton formation in the QD layer with the reduction of exciton leakage to the organic layer. The increased exciton recombination in QD layer results in better device performance, including efficiency and brightness.

To have a sustainable development of QD-LEDs, the cost and raw material supplies should also be taken into account. One of the main portions in the device fabrication cost comes from the transparent conducting electrode. Although tin-doped indium oxide (ITO) is widely used in research institutes and industry, the limited supply of indium sources has caused price of ITO to increase annually. Gallium-doped zinc oxide (GZO) was chosen as promising ITO-alternative candidate. In this study, transparent conductive GZO films were first deposited using radio frequency (RF) sputtering technique, followed by a high-temperature post-annealing process for a better film quality. Sheet resistance and resistivity of the GZO film are comparable to the commercially available ITO. Moreover, the QD-LEDs fabricated on GZO electrodes show similar performance to those prepared on ITO electrode. The results indicate that the indium-free ZnO-based transparent conducting electrode prepared by sputtering process can be a promising anode material for low-cost QD-LEDs.

8.2 Future Work

Although the research and development on QD-LEDs in the past five years have successfully demonstrated devices with improved internal quantum efficiency (IQE) and external quantum efficiency (EQE) level, there are numerous challenges that remained unsolved.

To date, near-unity IQE orange-red QD-LED device has been successfully demonstrated. However, highly efficient blue- and green-emitting QD-LEDs with near-unity IQE have still not been reported yet. Green and blue emission QDs have larger bandgap compared to the red QDs, making charge injection more difficult [45]. Besides, due to the deep HOMO of these QDs, choices of hole transport materials to effectively inject holes into these blue and green QDs are very limited. Therefore the study of hole transport materials whose energy bands match with QDs is still need to be carried on. The effective conduction and valence band of alloyed metal oxide films and oxide nanoparticles can be tuned by varying their composition and size, respectively. Therefore, they have great potentials to be a good charge transport materials [3, 65, 67].

In addition, currently most of the institutional and industrial research works use planar substrate for device fabrication. For planar device, a large amount of light is trapped inside the glass and the organic/ITO interface. It was predicted that only 20% of the light is extracted out from the planar devices. Introducing out-coupling layer at the interface can help to extract more light from the device and improve device performance several times over planar structures. There is, however, limited amount of research work on out-coupling layers to improve QD-LEDs' performance. It should also be noted that such out-coupling techniques are wavelength-dependent. Proper designs must be made so that it does not favor only certain range of wavelengths and suppress other wavelength ranges for light extraction, especially for white QD-LEDs.

Furthermore, all high-performance QD-LEDs reported to date use cadmium-based QDs, which are toxic and carcinogenic and require recycling. The presence of hazardous materials in QD-LEDs possesses safety concerns that could limit the commercialization of products even though it is very promising to provide highly efficient lighting to the society. Numerous research groups have addressed this issue and proposed cadmium-free QD-LEDs using less toxic indium phosphide (InP) and copper indium sulphide (CuInS) QDs [96, 121, 123, 149-152], however their performance is not yet comparable to those of cadmium-based QD-LEDs. As a result, high efficiency cadmium-free QD-LEDs could be one of the future directions.

Publication List

Journal Publications

- 1) Liu, S. W., Y. Divayana, X. W. Sun, Y. Wang, **K. S. Leck** and H. V. Demir (2011). "Improved performance of organic light-emitting diodes with MoO₃ interlayer by oblique angle deposition." **Optics Express** 19(5): 4513-4520.
- 2) Yang, X., Y. Divayana, D. Zhao, **K. S. Leck**, F. Lu, S. T. Tan, A. P. Abiyasa, Y. Zhao, H. V. Demir and X. W. Sun (2012). "A bright cadmium-free, hybrid organic/quantum dot white light-emitting diode." **Applied Physics Letters** 101(23): 233110.
- 3) Yang, X., D. Zhao, **K. S. Leck**, S. T. Tan, Y. X. Tang, J. Zhao, H. V. Demir and X. W. Sun (2012). "Full Visible Range Covering InP/ZnS Nanocrystals with High Photometric Performance and Their Application to White Quantum Dot Light-Emitting Diodes." **Advanced Materials** 24(30): 4180-4185.
- 4) **Leck, K. S.**, Y. Divayana, D. Zhao, X. Yang, A. P. Abiyasa, E. Mutlugun, Y. Gao, S. Liu, S. T. Tan, X. W. Sun and H. V. Demir (2013). "Quantum Dot Light-Emitting Diode with Quantum Dots Inside the Hole Transporting Layers." **ACS Applied Materials & Interfaces** 5(14): 6535-6540.
- 5) Yang, X., Y. Ma, E. Mutlugun, Y. Zhao, **K. S. Leck**, S. T. Tan, H. V. Demir, Q. Zhang, H. Du and X. W. Sun (2013). "Stable, Efficient, and All-Solution-Processed Quantum Dot Light-Emitting Diodes with Double-Sided Metal Oxide Nanoparticle Charge Transport Layers." **ACS Applied Materials & Interfaces** 6(1): 495-499.
- 6) Yang, X., Y. Tang, S. T. Tan, M. Bosman, Z. Dong, **K. S. Leck**, Y. Ji, H. V. Demir and X. W. Sun (2013). "Facile Synthesis of Luminescent AgInS₂-ZnS Solid Solution Nanorods." **Small** 9(16): 2689-2695.
- 7) Zhao, Y., R. Chen, Y. Gao, **K. S. Leck**, X. Yang, S. Liu, A. P. Abiyasa, Y. Divayana, E. Mutlugun, S. T. Tan, H. Sun, H. V. Demir and X. W. Sun (2013). "AC-driven, color- and brightness-tunable organic light-emitting diodes constructed from an electron only device." **Organic Electronics** 14(12): 3195-3200.
- 8) Yang, X., E. Mutlugun, Y. Zhao, Y. Gao, **K. S. Leck**, Y. Ma, L. Ke, S. T. Tan, H. V. Demir and X. W. Sun (2014). "Solution Processed Tungsten

Oxide Interfacial Layer for Efficient Hole-Injection in Quantum Dot Light-Emitting Diodes. **Small** 10(2): 247-252.

- 9) Zhao, Y., J. Zhang, S. Liu, Y. Gao, X. Yang, **K. S. Leck**, A. P. Abiyasa, Y. Divayana, E. Mutlugun, S. T. Tan, Q. Xiong, H. V. Demir and X. W. Sun (2014). "*Transition metal oxides on organic semiconductors.*" **Organic Electronics** 15(4): 871-877.
- 10) **Leck K. S.**; Mutlugun E.; Divayana Y.; Yang X.; Zhao Y.; Liu S.; Gao Y.; Fong K. E.; Tan S. T.; Dang C.; Sun X. W.; Demir H. V. "*Effective Interface Modification in Hybrid OrganicInorganic Quantum Dot-Light-Emitting Diodes Using Cs₂CO₃/Al Electrode*" in review.
- 11) Y. Wang, **K.S. Leck**, V.D. Ta, R. Chen, V. Nalla, Y. Gao, T. He, H.V. Demir, H. Sun, (2015) "*Blue Liquid Lasers from Solution of CdZnS/ZnS Ternary Alloy Quantum Dots with Quasi-Continuous Pumping*" **Advanced Materials** 27 (1), 169-175

Conference Presentations

- 1) K. S. Leck, Y. Divayana, D. W. Zhao, X. Yang, A. P. Abiyasa, E. Mutlugun, Y. Gao, S. W. Liu, S. T. Tan, X. W. Sun and H. V. Demir, "A Quantum-dot Light-emitting Diode with Quantum Dots Inside the Hole Transporting Layer", Symposium E: Solid-state devices for light emission and detection, **ICMAT 2013**.

Appendices

A) Synthesis of CdTe Nanocrystals in Aqueous Medium

Synthesis of cadmium telluride (CdTe) is carried out in aqueous solution using the given protocols [89]. The reaction can be separated into two mechanisms: (a) formation of CdTe precursors (Equation A.1) and (b) growth of CdTe nanocrystals (Equation A.2).

where R-SH stands for a thiol-based stabilizer, R represents as a hydrocarbon chain and S is sulphur atom.

In a typical synthesis, cadmium perchlorate hydrate ($Cd(ClO_4)_2 \cdot 6H_2O$, 99.5%, Alfa Aesar) is first dissolved in deionized (DI) water (Milli-Q water with resistivity of $18.2\ M\Omega \cdot cm$ at $25^\circ C$), followed by addition of thioglycolic acid (TGA, 98%, Fluka) which serves as stabilizing agent and the ligands. The addition of TGA makes the solution acidic (pH ~ 1.2), which is not suitable for high quality CdTe nanocrystal growth. Therefore, 1 M sodium hydroxide (NaOH, 50%, BestChem) is added dropwise to adjust the pH. Optimum pH for CdTe synthesis is around 12, and the solution is then changed from milky to colourless. The flask is subsequently connected to the Schlenk line and flown with Ar gas for 30 min to purge the oxygen. At the same time, in another flask,

aluminum telluride (Al_2Te_3 , lumps 99.5%, Cerac Inc.) is reacted with a certain amount of diluted sulfuric acid (H_2SO_4 , 98%, Schedelco) to generate hydrogen telluride (H_2Te) gas, which serves as a tellurium source and reacts with the cadmium source in the first flask. Other than the aluminum telluride, sodium hydrogen telluride (NaHTe) can also be used as a tellurium source in the synthesis, depending on the chemical availability. This reaction takes 30 min to complete for forming the CdTe precursor. After that, the precursor is heated up to 100 °C in open-air environment for desired time to obtain different sizes of CdTe nanocrystals. Due to the large amount of solvent being used in the reaction (more than 500 mL), heating may not be uniform in the reaction solution. Consequently the size distribution of nanocrystals for this synthesis is fairly large. Size-selected precipitation is normally performed to separate nanoparticles with particular sizes [153].

Figure A: CdTe nanocrystals taken at different time interval during synthesis (left) under roomlight and (right) under UV illumination.

References

1. Inter-Ministerial Committee on Sustainable Development, S., *A lively and liveable Singapore: strategies for sustainable growth*. 2009.
2. Hikmet, R.A.M., et al., *Polarized-Light-Emitting Quantum-Rod Diodes*. Advanced Materials, 2005. **17**(11): p. 1436-1439.
3. Lee, H., et al., *Improved Efficiency of Inverted Organic Light-Emitting Diodes Using Tin Dioxide Nanoparticles as an Electron Injection Layer*. ACS Applied Materials & Interfaces, 2013. **5**(6): p. 1977-1981.
4. Colvin, V.L., M.C. Schlamp, and A.P. Alivisatos, *Light-emitting diodes made from cadmium selenide nanocrystals and a semiconducting polymer*. Nature, 1994. **370**(6488): p. 354-357.
5. Cho, J., et al., *Fabrication of Highly Ordered Multilayer Films Using a Spin Self-Assembly Method*. Advanced Materials, 2001. **13**(14): p. 1076-1078.
6. Bae, W.K., et al., *Multicolored Light-Emitting Diodes Based on All-Quantum-Dot Multilayer Films Using Layer-by-Layer Assembly Method*. Nano Letters, 2010. **10**(7): p. 2368-2373.
7. Derby, B., *Inkjet Printing of Functional and Structural Materials: Fluid Property Requirements, Feature Stability, and Resolution*. Annual Review of Materials Research, 2010. **40**: p. 395-414.
8. Anikeeva, P.O., et al., *Quantum Dot Light-Emitting Devices with Electroluminescence Tunable over the Entire Visible Spectrum*. Nano Letters, 2009. **9**(7): p. 2532-2536.
9. Price, S.C., et al., *Studies of mist deposition for the formation of quantum dot CdSe films*. Semiconductor Science and Technology, 2009. **24**(10): p. 105024.
10. Conti, J.J., *International Energy Outlook 2013*. 2013, U.S. Energy Information Administration.
11. Black, R. *Lighting the key to energy saving* 2006; Available from: <http://news.bbc.co.uk/2/hi/science/nature/5128478.stm>.
12. Arik, M. and A. Setlur, *Environmental and economical impact of LED lighting systems and effect of thermal management*. International Journal of Energy Research, 2010. **34**(13): p. 1195-1204.
13. Schubert, E.F., *Light-emitting diodes*. 2006: Cambridge University Press.
14. Schanda, J. and I.C.o. Illumination, *Colorimetry: understanding the CIE system*. 2007: CIE/Commission internationale de l'eclairage.
15. *IKEA To Phase Out Incandescent Lighting In All US IKEA Stores Beginning August 1, 2010*. 2011 [cited 2013 10 October]; Available from: http://www.ikea.com/ms/en_US/about_ikea/press_room/press_release/national/phase_out_incandescent_lighting_press_release.html.

16. Boughey, D., *Phase-Out of Inefficient Incandescent Lamps and Standards for Compact Fluorescent Lamps* 2007, Australian Greenhouse Office: Australia.
17. KANTER, J. *Europe's Ban on Old-Style Bulbs Begins* August 31, 2009 [cited 2013 10 October]; Available from: <http://www.nytimes.com/2009/09/01/business/energy-environment/01iht-bulb.html>.
18. Phillips, J.M., et al., *Research challenges to ultra-efficient inorganic solid-state lighting*. Laser & Photonics Reviews, 2007. **1**(4): p. 307-333.
19. Craford, M.G., N. Holonyak, and F.A. Kish, *In pursuit of the ultimate lamp*. Scientific American, 2001. **284**(2): p. 62-67.
20. Visa, I., *Sustainable Energy in the Built Environment - Steps Towards nZEB: Proceedings of the Conference for Sustainable Energy (CSE) 2014*. 2014: Springer International Publishing.
21. Dupuis, P., et al. *LED lighting—Reduce the power consumption and increase the users comfort*. in *Industry Applications Society Annual Meeting, 2014 IEEE*. 2014. IEEE.
22. Dunlap, R., *Sustainable Energy, SI Edition*. 2014: Cengage Learning.
23. Holonyak, N. and S.F. Bevacqua, *Coherent (Visible) Light Emission From Ga(As_{1-x}P_x) Juncitons*. Applied Physics Letters, 1962. **1**(4): p. 82-83.
24. Wierer, J.J., A. David, and M.M. Megens, *III-nitride photonic-crystal light-emitting diodes with high extraction efficiency*. Nature Photonics, 2009. **3**(3): p. 163-169.
25. Dakin, J.P. and R.G.W. Brown, *Handbook of Optoelectronics (Two-Volume Set)*. 2010: Taylor & Francis.
26. *Cree Sets New R&D Performance Record with 276 Lumen-Per-Watt Power LED* 2013 February 13, 2013 [cited 2013 October 10]; Available from: <http://www.cree.com/News-and-Events/Cree-News/Press-Releases/2013/February/276-LPW>.
27. Hui, K.N., P.T. Lai, and H.W. Choi, *Vertically-stacked color-tunable LEDs*. physica status solidi (c), 2009. **6**(S2): p. S902-S904.
28. Hui, K.N., et al., *Design of vertically-stacked polychromatic light-emitting diodes*. Optics Express, 2009. **17**(12): p. 9873-9878.
29. Crawford, M.H., *LEDs for Solid-State Lighting: Performance Challenges and Recent Advances*. IEEE Journal of Selected Topics in Quantum Electronics, 2009. **15**(4): p. 1028-1040.
30. Graydon, O., *The new oil?* Nature Photonics, 2011. **5**(1): p. 1-1.
31. Erdem, T., et al., *A photometric investigation of ultra-efficient LEDs with high color rendering index and high luminous efficacy employing nanocrystal quantum dot luminophores*. Optics Express, 2010. **18**(1): p. 340-347.
32. Nizamoglu, S., et al., *Warm-white light-emitting diodes integrated with colloidal quantum dots for high luminous efficacy and color rendering*. Optics Letters, 2010. **35**(20): p. 3372-3374.

33. Wood, V. and V. Bulović, *Colloidal quantum dot light-emitting devices*. Nano Reviews, 2010. **1**(1).
34. Pope, M., H.P. Kallmann, and P. Magnante, *Electroluminescence in Organic Crystals*. The Journal of Chemical Physics, 1963. **38**(8): p. 2042-2043.
35. Shirakawa, H., et al., *Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH)*. Journal of the Chemical Society, Chemical Communications, 1977(16): p. 578-580.
36. Heeger, A.J., *Semiconducting and metallic polymers: the fourth generation of polymeric materials (Nobel lecture)*. Angewandte Chemie International Edition, 2001. **40**(14): p. 2591-2611.
37. Heeger, A.J., *Nobel Lecture: Semiconducting and metallic polymers: The fourth generation of polymeric materials*. Reviews of Modern Physics, 2001. **73**(3): p. 681-700.
38. Tang, C.W., S.A. VanSlyke, and C.H. Chen, *Electroluminescence of doped organic thin films*. Journal of Applied Physics, 1989. **65**(9): p. 3610-3616.
39. Tang, C.W. and S.A. VanSlyke, *Organic electroluminescent diodes*. Applied Physics Letters, 1987. **51**(12): p. 913-915.
40. Reineke, S., et al., *White organic light-emitting diodes with fluorescent tube efficiency*. Nature, 2009. **459**(7244): p. 234-238.
41. van Gemmern, P., et al., *Influence of carrier conductivity and injection on efficiency and chromaticity in small-molecule white organic light-emitting diodes based on 4,4'-bis(2,2'-diphenylvinyl)-1,1'-spirobiphenyl and rubrene*. Journal of Applied Physics, 2006. **100**(12): p. -.
42. Talapin, D.V., et al., *Prospects of Colloidal Nanocrystals for Electronic and Optoelectronic Applications*. Chemical Reviews, 2009. **110**(1): p. 389-458.
43. Kwak, J., et al., *Bright and Efficient Full-Color Colloidal Quantum Dot Light-Emitting Diodes Using an Inverted Device Structure*. Nano Letters, 2012. **12**(5): p. 2362-2366.
44. Panzer, M.J., et al., *Nanoscale Morphology Revealed at the Interface Between Colloidal Quantum Dots and Organic Semiconductor Films*. Nano Letters, 2010. **10**(7): p. 2421-2426.
45. Wood, V., et al., *Selection of Metal Oxide Charge Transport Layers for Colloidal Quantum Dot LEDs*. ACS Nano, 2009. **3**(11): p. 3581-3586.
46. Kim, T.-H., et al., *Full-colour quantum dot displays fabricated by transfer printing*. Nature Photonics, 2011. **5**(3): p. 176-182.
47. Lim, J., et al., *Perspective on synthesis, device structures, and printing processes for quantum dot displays*. Optical Materials Express, 2012. **2**(5): p. 594-628.
48. Jang, E., et al., *White-Light-Emitting Diodes with Quantum Dot Color Converters for Display Backlights*. Advanced Materials, 2010. **22**(28): p. 3076-3080.

49. Vision, Q. *Color IQ*. 2013 [cited 2013 10 October]; Available from: <http://www.qdvision.com/quantum-light-platform>.
50. Sony. 2013: <http://www.sony.co.uk/hub/lcd-television/benefits/tv-picture-quality>. p. Sony Bravia LED TV with triluminous display technology.
51. Cheng, K.-Y., et al., *High-Efficiency Silicon Nanocrystal Light-Emitting Devices*. Nano Letters, 2011. **11**(5): p. 1952-1956.
52. Anikeeva, P.O., et al., *Electronic and excitonic processes in light-emitting devices based on organic materials and colloidal quantum dots*. Physical Review B, 2008. **78**(8): p. 085434.
53. Cho, K.-S., et al., *High-performance crosslinked colloidal quantum-dot light-emitting diodes*. Nature Photonics, 2009. **3**(6): p. 341-345.
54. Tan, Z., et al., *Bright and Color-Saturated Emission from Blue Light-Emitting Diodes Based on Solution-Processed Colloidal Nanocrystal Quantum Dots*. Nano Letters, 2007. **7**(12): p. 3803-3807.
55. Sun, Q., et al., *Bright, multicoloured light-emitting diodes based on quantum dots*. Nature Photonics, 2007. **1**(12): p. 717-722.
56. Qian, L., et al., *Stable and efficient quantum-dot light-emitting diodes based on solution-processed multilayer structures*. Nature Photonics, 2011. **5**(9): p. 543-548.
57. Yang, X., et al., *Full Visible Range Covering InP/ZnS Nanocrystals with High Photometric Performance and Their Application to White Quantum Dot Light-Emitting Diodes*. Advanced Materials, 2012. **24**(30): p. 4180-4185.
58. Schlamp, M.C., X. Peng, and A.P. Alivisatos, *Improved efficiencies in light emitting diodes made with CdSe(CdS) core/shell type nanocrystals and a semiconducting polymer*. Journal of Applied Physics, 1997. **82**(11): p. 5837-5842.
59. Kwon, B.W., et al., *Solution-Processed White Light-Emitting Diode Utilizing Hybrid Polymer and Red, Green & Blue Quantum Dots*. Japanese Journal of Applied Physics, 2012. **51**: p. 09MH03.
60. Coe, S., et al., *Electroluminescence from single monolayers of nanocrystals in molecular organic devices*. Nature, 2002. **420**(6917): p. 800-803.
61. Woo, W.K., et al., *Reversible Charging of CdSe Nanocrystals in a Simple Solid-State Device*. Advanced Materials, 2002. **14**(15): p. 1068-1071.
62. Shirasaki, Y., et al., *Emergence of colloidal quantum-dot light-emitting technologies*. Nature Photonics, 2013. **7**(1): p. 13-23.
63. Caruge, J.M., et al., *NiO as an inorganic hole-transporting layer in quantum-dot light-emitting devices*. Nano Letters, 2006. **6**(12): p. 2991-2994.
64. Caruge, J.M., et al., *Colloidal quantum-dot light-emitting diodes with metal-oxide charge transport layers*. Nature Photonics, 2008. **2**(4): p. 247-250.

65. Yang, X., et al., *Solution Processed Tungsten Oxide Interfacial Layer for Efficient Hole-Injection in Quantum Dot Light-Emitting Diodes*. Small, 2013: p. n/a-n/a.
66. Lee, K.-H., et al., *Highly Efficient, Color-Pure, Color-Stable Blue Quantum Dot Light-Emitting Devices*. ACS Nano, 2013. **7**(8): p. 7295-7302.
67. Mashford, B.S., et al., *High-efficiency quantum-dot light-emitting devices with enhanced charge injection*. Nature Photonics, 2013. **7**(5): p. 407-412.
68. Ponce, F.A. and D.P. Bour, *Nitride-based semiconductors for blue and green light-emitting devices*. Nature, 1997. **386**(6623): p. 351-359.
69. Michalet, X., et al., *Quantum Dots for Live Cells, in Vivo Imaging, and Diagnostics*. Science, 2005. **307**(5709): p. 538-544.
70. Byers, R.J. and E.R. Hitchman, *Quantum Dots Brighten Biological Imaging*. Progress in Histochemistry and Cytochemistry, 2011. **45**(4): p. 201-237.
71. Raffaele, R.P., et al., *Quantum dot solar cells*. Progress in Photovoltaics: Research and Applications, 2002. **10**(6): p. 433-439.
72. Brus, L.E., *A simple model for the ionization potential, electron affinity, and aqueous redox potentials of small semiconductor crystallites*. The Journal of Chemical Physics, 1983. **79**(11): p. 5566-5571.
73. Gaponenko, S.V., *Introduction to Nanophotonics*. 2010: Cambridge University Press.
74. Lu, Z., *Methodologies to enhance the resolution of electron beam lithography for nanostructure fabrication*. 2007, State University of New York at Buffalo: Ann Arbor. p. 190.
75. Palankar, R., et al., *Fabrication of Quantum Dot Microarrays Using Electron Beam Lithography for Applications in Analyte Sensing and Cellular Dynamics*. ACS Nano, 2013. **7**(5): p. 4617-4628.
76. Yang, X., et al., *Breaking the feature sizes down to sub-22 nm by plasmonic interference lithography using dielectric-metal multilayer*. Optics Express, 2009. **17**(24): p. 21560-21565.
77. Silverman, J.P., *Challenges and progress in x-ray lithography*. Journal of Vacuum Science & Technology B, 1998. **16**(6): p. 3137-3141.
78. Massimo, F.B., et al., *Quantum dots by ultraviolet and x-ray lithography*. Nanotechnology, 2007. **18**(31): p. 315603.
79. Gan, Z., et al., *Three-dimensional deep sub-diffraction optical beam lithography with 9 nm feature size*. Nat Commun, 2013. **4**.
80. Costner, E.A., et al., *Nanoimprint Lithography Materials Development for Semiconductor Device Fabrication*. Annual Review of Materials Research, 2009. **39**: p. 155-180.
81. Stiles, P.L., *Direct deposition of micro- and nanoscale hydrogels using Dip Pen Nanolithography (DPN)*. Nature Methods, 2010. **7**(8): p. I-II.

82. Bhattacharya, P., S. Ghosh, and A.D. Stiff-Roberts, *Quantum Dot Opto-electronic Devices*. Annual Review of Materials Research, 2004. **34**(1): p. 1-40.
83. Choi, C.L. and A.P. Alivisatos, *From Artificial Atoms to Nanocrystal Molecules: Preparation and Properties of More Complex Nanostructures*. Annual Review of Physical Chemistry, 2010. **61**: p. 369-389.
84. Peng, Z.A. and X. Peng, *Formation of High-Quality CdTe, CdSe, and CdS Nanocrystals Using CdO as Precursor*. Journal of the American Chemical Society, 2000. **123**(1): p. 183-184.
85. LaMer, V.K. and R.H. Dinegar, *Theory, Production and Mechanism of Formation of Monodispersed Hydrosols*. Journal of the American Chemical Society, 1950. **72**(11): p. 4847-4854.
86. Rogach, A.L., et al., *Organization of Matter on Different Size Scales: Monodisperse Nanocrystals and Their Superstructures*. Advanced Functional Materials, 2002. **12**(10): p. 653-664.
87. Murray, C.B., C.R. Kagan, and M.G. Bawendi, *Synthesis And Characterization of Monodisperse Nanocrystals and Close-packed Nanocrystal Assemblies*. Annual Review of Materials Science, 2000. **30**(1): p. 545-610.
88. Donega, C.D., *Synthesis and properties of colloidal heteronanocrystals*. Chemical Society Reviews, 2011. **40**(3): p. 1512-1546.
89. Rogach, A.L., et al., *Aqueous Synthesis of Thiol-Capped CdTe Nanocrystals: State-of-the-Art*. The Journal of Physical Chemistry C, 2007. **111**(40): p. 14628-14637.
90. Peng, X., et al., *Shape control of CdSe nanocrystals*. Nature, 2000. **404**(6773): p. 59-61.
91. Peng, X., et al., *Epitaxial Growth of Highly Luminescent CdSe/CdS Core/Shell Nanocrystals with Photostability and Electronic Accessibility*. Journal of the American Chemical Society, 1997. **119**(30): p. 7019-7029.
92. Klimov, V.I., et al., *Single-exciton optical gain in semiconductor nanocrystals*. Nature, 2007. **447**(7143): p. 441-446.
93. Demir, H.V., et al., *Quantum dot integrated LEDs using photonic and excitonic color conversion*. Nano Today, 2011. **6**(6): p. 632-647.
94. Chang, M.-Y., et al., *High-Color-Purity Organic Light-Emitting Diodes Incorporating a Cyanocoumarin-Derived Red Dopant Material*. Journal of The Electrochemical Society, 2008. **155**(12): p. J365-J370.
95. Wood, V., et al., *Air-Stable Operation of Transparent, Colloidal Quantum Dot Based LEDs with a Unipolar Device Architecture*. Nano Letters, 2009. **10**(1): p. 24-29.
96. Lim, J., et al., *Highly Efficient Cadmium-Free Quantum Dot Light-Emitting Diodes Enabled by the Direct Formation of Excitons within InP@ZnSeS Quantum Dots*. ACS Nano, 2013. **7**(10): p. 9019-9026.

97. Bae, W.K., et al., *Highly Efficient Green-Light-Emitting Diodes Based on CdSe@ZnS Quantum Dots with a Chemical-Composition Gradient*. *Advanced Materials*, 2009. **21**(17): p. 1690-1694.
98. Zhong, X., et al., *Composition-Tunable ZnxCd1-xSe Nanocrystals with High Luminescence and Stability*. *Journal of the American Chemical Society*, 2003. **125**(28): p. 8589-8594.
99. Li, J.J., et al., *Large-Scale Synthesis of Nearly Monodisperse CdSe/CdS Core/Shell Nanocrystals Using Air-Stable Reagents via Successive Ion Layer Adsorption and Reaction*. *Journal of the American Chemical Society*, 2003. **125**(41): p. 12567-12575.
100. Yu, W.W. and X. Peng, *Formation of High-Quality CdS and Other II-VI Semiconductor Nanocrystals in Noncoordinating Solvents: Tunable Reactivity of Monomers*. *Angewandte Chemie International Edition*, 2002. **41**(13): p. 2368-2371.
101. Yu, W.W., et al., *Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals*. *Chemistry of Materials*, 2003. **15**(14): p. 2854-2860.
102. Sapra, S. and D.D. Sarma, *Evolution of the electronic structure with size in II-VI semiconductor nanocrystals*. *Physical Review B*, 2004. **69**(12): p. 125304.
103. Chen, O., et al., *Compact high-quality CdSe-CdS core-shell nanocrystals with narrow emission linewidths and suppressed blinking*. *Nature Materials*, 2013. **12**(5): p. 445-451.
104. Bae, W.K., et al., *Single-Step Synthesis of Quantum Dots with Chemical Composition Gradients*. *Chemistry of Materials*, 2008. **20**(2): p. 531-539.
105. Grabolle, M., et al., *Determination of the Fluorescence Quantum Yield of Quantum Dots: Suitable Procedures and Achievable Uncertainties*. *Analytical Chemistry*, 2009. **81**(15): p. 6285-6294.
106. Rurack, K. and M. Spieles, *Fluorescence Quantum Yields of a Series of Red and Near-Infrared Dyes Emitting at 600-1000 nm*. *Analytical Chemistry*, 2011. **83**(4): p. 1232-1242.
107. Hamamatsu, *Quantaaurus-QY C11347-11*. 2013: <http://www.hamamatsu.com/jp/en/product/category/5001/5009/5033/C11347-11/index.html>.
108. Würth, C., et al., *Relative and absolute determination of fluorescence quantum yields of transparent samples*. *Nat. Protocols*, 2013. **8**(8): p. 1535-1550.
109. Olmsted, J., *Calorimetric determinations of absolute fluorescence quantum yields*. *The Journal of Physical Chemistry*, 1979. **83**(20): p. 2581-2584.
110. Leck, K.S., et al., *Quantum Dot Light-Emitting Diode with Quantum Dots Inside the Hole Transporting Layers*. *ACS Applied Materials & Interfaces*, 2013. **5**(14): p. 6535-6540.

111. Hameed, T.A.S., R. Baiju, and P. Predeep, *Organic Light Emitting Diodes: Device Physics and Effect of Ambience on Performance Parameters*. 2011: INTECH Open Access Publisher.
112. Xie, G., et al., *Very low turn-on voltage and high brightness tris-(8-hydroxyquinoline) aluminum-based organic light-emitting diodes with a MoOx-p-doping layer*. Applied Physics Letters, 2008. **92**(9): p. 093305.
113. Forrest, S.R., D.D.C. Bradley, and M.E. Thompson, *Measuring the Efficiency of Organic Light-Emitting Devices*. Advanced Materials, 2003. **15**(13): p. 1043-1048.
114. Fairchild, M.D., *Color appearance models*. 2005: J. Wiley.
115. Lennie, P., J. Pokorny, and V.C. Smith, *Luminance*. Journal of the Optical Society of America A, 1993. **10**(6): p. 1283-1293.
116. Stouwdam, J.W. and R.A.J. Janssen, *Electroluminescent Cu-doped CdS Quantum Dots*. Advanced Materials, 2009. **21**(28): p. 2916-2920.
117. Qian, L., et al., *Stable and efficient quantum-dot light-emitting diodes based on solution-processed multilayer structures*. Nat Photon, 2011. **5**(9): p. 543-548.
118. Cho, K.-S., et al., *High-performance crosslinked colloidal quantum-dot light-emitting diodes*. Nat Photon, 2009. **3**(6): p. 341-345.
119. Zhang, Y., et al., *Employing Heavy Metal-Free Colloidal Quantum Dots in Solution-Processed White Light-Emitting Diodes*. Nano Letters, 2010. **11**(2): p. 329-332.
120. Schreuder, M.A., et al., *White Light-Emitting Diodes Based on Ultrasmall CdSe Nanocrystal Electroluminescence*. Nano Letters, 2010. **10**(2): p. 573-576.
121. Yang, X., et al., *A bright cadmium-free, hybrid organic/quantum dot white light-emitting diode*. Applied Physics Letters, 2012. **101**(23): p. 233110.
122. Sun, Q.J., et al., *White light from polymer light-emitting diodes: Utilization of fluorenone defects and exciplex*. Applied Physics Letters, 2006. **88**(16): p. -.
123. Shen, H., et al., *Highly efficient blue-green quantum dot light-emitting diodes using stable low-cadmium quaternary-alloy ZnCdSSe/ZnS core/shell nanocrystals*. ACS Applied Materials & Interfaces, 2013. **5**(10): p. 4260-4265.
124. Kang, J.-W., et al., *Low roll-off of efficiency at high current density in phosphorescent organic light emitting diodes*. Applied Physics Letters, 2007. **90**(22): p. 223508.
125. Tse, S.C., K.C. Kwok, and S.K. So, *Electron transport in naphthylamine-based organic compounds*. Applied Physics Letters, 2006. **89**(26): p. 262102.
126. Klenkler, R.A. and G. Voloshin, *Hole and Electron Transport in Triarylamine-Based Charge-Transport Materials Investigated by the Time-of-Flight Method*. The Journal of Physical Chemistry C, 2011. **115**(34): p. 16777-16781.

127. Zhao, J., et al., *Efficient CdSe/CdS Quantum Dot Light-Emitting Diodes Using a Thermally Polymerized Hole Transport Layer*. Nano Letters, 2006. **6**(3): p. 463-467.
128. Yang, X., et al., *Solution Processed Tungsten Oxide Interfacial Layer for Efficient Hole-Injection in Quantum Dot Light-Emitting Diodes*. Small, 2014. **10**(2): p. 247-252.
129. Borg, L.z., et al., *The effect of band gap alignment on the hole transport from semiconducting block copolymers to quantum dots*. Journal of Materials Chemistry C, 2013. **1**(9): p. 1722-1726.
130. Kido, J. and T. Matsumoto, *Bright organic electroluminescent devices having a metal-doped electron-injecting layer*. Applied Physics Letters, 1998. **73**(20): p. 2866-2868.
131. Xu, Q., et al., *Ultrahigh efficiency green polymer light-emitting diodes by nanoscale interface modification*. Applied Physics Letters, 2003. **83**(23): p. 4695-4697.
132. Mori, T., et al., *Electronic structure of 8-hydroxyquinoline aluminum/LiF/Al interface for organic electroluminescent device studied by ultraviolet photoelectron spectroscopy*. Applied Physics Letters, 1998. **73**(19): p. 2763-2765.
133. Parthasarathy, G., et al., *Lithium doping of semiconducting organic charge transport materials*. Journal of Applied Physics, 2001. **89**(9): p. 4986-4992.
134. Walzer, K., et al., *Highly Efficient Organic Devices Based on Electrically Doped Transport Layers*. Chemical Reviews, 2007. **107**(4): p. 1233-1271.
135. Huang, J., Z. Xu, and Y. Yang, *Low-Work-Function Surface Formed by Solution-Processed and Thermally Deposited Nanoscale Layers of Cesium Carbonate*. Advanced Functional Materials, 2007. **17**(12): p. 1966-1973.
136. Zhao, J., et al., *The role of cesium carbonate on the electron injection and transport enhancement in organic layer by admittance spectroscopy*. Applied Physics Letters, 2012. **101**(19): p. 193303
137. Zhao, D.W., et al., *An inverted organic solar cell with an ultrathin Ca electron-transporting layer and MoO₃ hole-transporting layer*. Applied Physics Letters, 2009. **95**(15): p. 153304.
138. Oyamada, T., et al., *Efficient Electron Injection Mechanism in Organic Light-Emitting Diodes Using an Ultra Thin Layer of Low-Work-Function Metals*. Japanese Journal of Applied Physics. **42**(Part 2, No. 12B): p. L1535.
139. Wu, C.C., et al., *Poly(p-phenylene vinylene)/tris(8-hydroxy) quinoline aluminum heterostructure light emitting diode*. Applied Physics Letters, 1995. **66**(6): p. 653-655.
140. Ho, M.D., et al., *Polymer and Small Molecule Mixture for Organic Hole Transport Layers in Quantum Dot Light-Emitting Diodes*. ACS Applied Materials & Interfaces, 2013.

141. Yang, X., et al., *Stable, Efficient, and All-Solution-Processed Quantum Dot Light-Emitting Diodes with Double-Sided Metal Oxide Nanoparticle Charge Transport Layers*. ACS Applied Materials & Interfaces, 2013.
142. Wei, H.H.-Y., et al., *Colloidal Semiconductor Quantum Dots with Tunable Surface Composition*. Nano Letters, 2012. **12**(9): p. 4465-4471.
143. Bhosle, V., A. Tiwari, and J. Narayan, *Metallic conductivity and metal-semiconductor transition in Ga-doped ZnO*. Applied Physics Letters, 2006. **88**(3): p. -.
144. Ellmer, K., *Past achievements and future challenges in the development of optically transparent electrodes*. Nature Photonics, 2012. **6**(12): p. 809-817.
145. Bhosle, V., et al., *Gallium-doped zinc oxide films as transparent electrodes for organic solar cell applications*. Journal of Applied Physics, 2007. **102**(2): p. -.
146. Dutta, T., et al., *High work function (p-type NiO 1+ x)/Zn 0.95 Ga 0.05 O heterostructures for transparent conducting oxides*. Journal of Physics D: Applied Physics, 2010. **43**(10): p. 105301.
147. Park, K.C., D.Y. Ma, and K.H. Kim, *The physical properties of Al-doped zinc oxide films prepared by RF magnetron sputtering*. Thin Solid Films, 1997. **305**(1-2): p. 201-209.
148. Bhosle, V., A. Tiwari, and J. Narayan, *Electrical properties of transparent and conducting Ga doped ZnO*. Journal of Applied Physics, 2006. **100**(3): p. -.
149. Sharma, V.K., et al., *Tunable White-Light-Emitting Mn-Doped ZnSe Nanocrystals*. ACS Applied Materials & Interfaces, 2014.
150. Wang, L., et al., *Common Origin of Green Luminescence in Carbon Nanodots and Graphene Quantum Dots*. ACS Nano, 2014.
151. Kwon, W., et al., *Electroluminescence from Graphene Quantum Dots Prepared by Amidative Cutting of Tattered Graphite*. Nano Letters, 2014.
152. Zhang, W., et al., *Color-Tunable Highly Bright Photoluminescence of Cadmium-Free Cu-Doped Zn-In-S Nanocrystals and Electroluminescence*. Chemistry of Materials, 2013. **26**(2): p. 1204-1212.
153. Kowalczyk, B., I. Lagzi, and B.A. Grzybowski, *Nanoseparations: Strategies for size and/or shape-selective purification of nanoparticles*. Current Opinion in Colloid & Interface Science, 2011. **16**(2): p. 135-148.