Abstract

Quantum dot light-emitting diode (QLED) attracted much attention for the next generation of display due to its advantages in high color saturation, tunable color emission, and high stability. Compared with traditional LED display, QLED display has advantages in flexible and robust application, which makes wearable and stretchable display possible in the future. In addition, QLED display is a self-emissive display, in which light is generated by individual subpixel, each subpixel can be individually controlled. Each subpixel in LED display is constituted by liquid crystal and color filter, which make LED display have lower power efficiency and less enhanced functionality. This chapter introduces the QLED based on the QLED structure and light-emitting mechanism of QLED. Then, a novel method for fabricating QLEDs, which is based on the ZnO nanoparticles (NPs) incorporated into QD nanoparticles, will be introduced. The QLED device was fabricated by all-solution processes, which make the QLED fabrication process more flexible and more suitable for industrialization. What is more, as QLED devices were planned to integrate into a display, all-solution fabrication processes also make printing QLED display device possible in the near future.

Keywords: quantum dots, light-emitting diode, display, quantum dot light-emitting diode, material, printing

1. Introduction

After QLED was first published in 1994, a lot effort had been spent to improve the reliability and performance of QLED devices [1, 2]. The first QLED device uses thick QDs acting as both the emission layer and electron transport layer, which can be referred to in Figure 1(a) and (b). The luminous efficiency of QLED device has been improved by the use of electron injection layer. Coe et al. published a sandwiched QLED structure in 2002, which consisted of two organic thin films with QDs as the emission layer. The luminescence was improved 25-fold over the best results of the previous QLED device, as shown in Figure 1(d) [3]. The QLEDs use Alq3 and poly-TPD as the electron transport layer, as shown in Figure 1(c). However, the organic thin layers were sensitive to moisture and oxygen. Thus, replacing organic material with inorganic material seems to be the best solution to improve the reliability of the QLED device. Mueller et al. fabricated an all-inorganic
Figure 1.
Structure designs and material designs for efficient QLEDs. (a) Energy-level structure of the first QLED. (b) Electroluminescence of the first QLED [1]. (c) Electroluminescence spectra and structures for a 40-nm-thick film of Alq3, followed by a 75-nm-thick Mg:Ag cathode with a 50 nm Ag cap. (d) The corresponding external quantum efficiency [3]. (e) QLED structure consists of p-type GaN and n-type GaN. (f) Electroluminescence of QLED consists of p-type GaN and n-type GaN [4]. (g) QLED structure with metal oxide as the electron transport layer with layer-by-layer structure in emission layer. (h) Electroluminescence and photoluminescence of the QLED with metal oxide as the electron transport layer with layer-by-layer structure in emission layer [5].
QLED in which QDs were sandwiched by n-type GaN and p-type GaN. Figure 1(e) shows the structure of QLED with GaN, while Figure 1(f) shows the corresponding electrical performance. Mueller et al. used metal-organic chemical vapor deposition (MOCVD) method to deposit n-type GaN and p-type GaN [4]. However, the deposition method is too harsh for QDs that make the luminescence efficiency lower than the first type of QLED device. Then in 2010, Bendall et al. demonstrated an all-inorganic QLED with metal oxide as the electron transport layer. The QLED had a layer-by-layer structure, which had three-layer emission layers as shown in Figure 1(g) and (h) [5]. The overall device performance was still poor which is caused by the degradation of QDs during the harsh deposition process of inorganic materials. However, these devices showed condescending stability under long-term usage and high current density conditions.

The organic materials had an advantage of high luminescence, while inorganic materials had an advantage of high reliability. Then the researcher combined the advantage of both organic materials and inorganic materials by using both organic materials and inorganic materials as the electron transport layers. MoS$_2$, NiO, TiO$_2$, and ZnO have been reported as the inorganic charge transport layers (CTLs) [6–8].

According to the type of electron transport layers, the structure of QLEDs can be categorized into four different types (Figure 2): (a) organic/QD bilayer, (b) all-organic electron transport layer, (c) all-inorganic electron transport layer, and (d) organic/inorganic electron transport layer. The four different types of QLED structure also represent the development history of QLEDs in sequence.

Among these four types of QLED structure, inorganic materials are one of the most important choices for electron transport layers owing to their high electrical conductivity and good stability against environmental factors such as oxygen and moisture. ZnO nanoparticles (NPs) applied in electron transport layer are a significant breakthrough in QLED development history, due to their excellent electron

![Figure 2](image-url)

Four representative QLED structure types based on electron transport layers. (a) Organic polymer electron transport layer, (b) all-organic polymer electron transport layer, (c) all-inorganic electron transport layer, and (d) organic/inorganic electron transport layer [1–10].
mobility and no significant damage to the underlying QD layer during fabrication process. What’s more, ZnO NPs are compatible with both polar solvent and nonpolar solvent, which makes the QLED fabrication process more flexible. More details about ZnO NPs will be introduced in Section 3.

2. Light emission mechanism of QLED

The emission mechanism of QLED is discussed in this subsection. A QLED has a similar structure and behavior as an OLED. In the QLED, the emitter is a semiconductor nanoparticle, while in the OLED, the emitter is an organic material.

2.1 Electron molecular orbital

Once a molecular orbital achieved the maximum electron energy, it is called the highest occupied molecular orbital (HOMO). Otherwise, if a molecular orbital has unfilled electrons, the molecular orbital is called the lowest unoccupied molecular orbital (LUMO). The energies of HOMO and LUMO affect the ionization potential and electron affinity of materials (Figure 3) [12].

Ionization potential energy is the minimum energy required to extract one electron from the HOMO, and electron affinity is the energy required to add one electron to the LUMO so that the system is stabilized [11, 12].

Before considering the light emission mechanism, it is important to understand the electron configuration in both the ground state and the excited state. Before excitation, when in ground state, the electrons are placed with both upward spin and downward spin (Figure 3). When excited, the electrons in the upper state are allocated with the same spin state, or the spin is reversed. The light emission is resulting from the energy transfer from the excitation state to the ground state.

2.2 Electron transfer and recombination

Normal materials in QLED have high resistance at weak electric fields. Therefore, researchers introduced the thin film to create strong electric field and chose
structures and materials suitable for charge injection [13]. The QLED performance is highly dependent on the choice of charge injection materials. Good charge injection materials should have high carrier mobility and balance the electron/hole injections well. The charge injection from electrodes follows the Schottky effect that means the injection barrier would be lowered according to the image force principle.

When an electron is injected into the electrode, if all the HOMO orbitals are occupied and cannot accept the additional charge, the charge will be transferred into the LUMO. When electrons are transferred into the LUMO, they form an electric current. At the same time, there will be a hole injected from the anode electrode which will be transferred into the HOMO. However, when the amount of injected charge exceeds the internal charge amount, the conduction system changes from ohmic to “space charge-limited current” [12–14].

If charge transfer by electric field and diffusion is taken into account and no trap is assumed, the electric current can be expressed as Eq. (1):

$$ J = \frac{9 \varepsilon \mu V^2}{8 d^3} $$

According to Eq. (1), the electric current is proportional to the square of the voltage. This is called the Mott-Gurney law, an extension of Child’s law that takes collision into consideration [15].

The recombination and generation of excitons of QLED are shown in Figure 4.

When an electron and a hole recombined in the emission layer, the photons formed, whose wavelength corresponds to the energy bandgap of the quantum dots. The more electron and hole are recombined, the more photos will be generated, which corresponds to more light we could detect. Thus, people applied the hole transport layer (HTL) and electron transport layer (ETL) to restrict the electrons and holes in the emission layer, in order to improve the device efficiency.

There are five typical layers for a QLED structure:

- Electron transport layer (ETL)—for electron injection from the cathode and transportation of the electron.
- Electron injection layer (EIL)—for electron injection from the cathode electrode.
- Hole transport layer (HTL)—for hole transportation from HIL to EML.

![Figure 4. The energy diagram of QLED.](image)
• Hole injection layer (HIL)—for hole injection from the anode electrode.

• Emission layer (EML)—electron/hole transportation and their recombination to form an exciton; this is the QD layer in QLED.

This direct injection of charge carriers is assumed as the most common phenomenon for creating an exciton in the device.

In Section 1, the QLED structure types are elaborated. Thus, it is very important to design a QLED by factoring in the relationships between the work function of each layer. The QLED device fabrication process will be discussed in Section 3.

2.3 ZnO nanoparticles

Behind the QLED structure, the ZnO nanoparticles (ZnO NPs) have gained substantial interest in the research community as the charge transport layer (CTL). In 2008, Janssen [8] and co-workers demonstrated all-solution-processed multilayer QLEDs by using ZnO NPs as ETLs and organic materials as HTLs. The colloidal ZnO NPs were dispersed in isopropanol, and the deposition of the ZnO NPs on the top of the QD layers did not dissolve the underlying layers. Since then, continuous efforts were made to improve the performance of QLED with solution-processed n-type oxides as CTLs. ZnO NPs are widely used as CTLs in the state of the art of high-performance QLEDs.

Generally, solution-processed oxide CTLs can be deposited by two approaches, the precursor approach and the nanocrystal approach. The molar ratio of zinc precursor to potassium hydroxide (KOH) played an important role in determining the shape of ZnO NPs and hence affected the conductivity and mobility of ZnO NP film prepared from ZnO NPs [15–17]. ZnO NPs were synthesized by hydrolysis/condensation reactions under basic conditions. The synthesis procedure will be introduced in Section 3.

3. QLED fabrication by spin coating

3.1 Experimental chemicals

Detergent TFD4 was purchased from BioLab, PEDOT:PSS 4083 from Heraeus, poly-TPD (LT-N149) from Luminescence Technology Corp Ltd., patterned ITO glass from Xinyan Technology Ltd., green (CdZnSeS/ZnS) quantum dots from Suzhou Mesolight Inc., and zinc acetate dihydrate powder, potassium hydroxide flakes, acetone, isopropyl alcohol, methyl alcohol, chloroform, and chlorobenzene all from Aldrich.

3.2 Synthesis of ZnO nanoparticles

The uncleation-dissolution-recrystallization growth method [16] was applied to synthesize the ZnO nanoparticles. Firstly 0.37 g potassium hydroxide was dissolved in 16.25 ml methyl alcohol. Then zinc acetate dihydrate solution was prepared by adding 0.74 g zinc acetate dihydrate in 31.25 ml methyl alcohol at 60°C under vigorous stirring. Then the potassium hydroxide solution was jetted into the zinc acetate dihydrate solution at the rate of 0.8 ml/min. The reaction takes around 1.7 h under N₂ protection condition. After the reaction, the solution was allowed to sit for another 2 h to let the ZnO nanoparticles settle at the bottom of the reaction flask. The ZnO nanoparticles were washed twice by methyl alcohol. Then the ZnO
nanoparticles were dispersed in chloroform and isopropyl alcohol mix solution at the concentration of 35 mg/ml.

Transmission electron microscopy (TEM, JEOL JEM 2010) was applied to characterize the morphology of the nanoparticles.

### 3.3 QLED device preparation

The patterned ITO glass was cleaned by detergent, methyl alcohol, acetone, and isopropyl alcohol in turn, each sonication for 20 minutes. After cleaning, UV ozone plasma was applied for surface energy modification. PEDOT:PSS was spin-coated on the cleaned ITO surface at 3000 rpm for 30 s and then baked under vacuum at 150°C for 30 min. Then hole transport layer (HTL) was prepared by spin coating poly-TPD on the annealed PEDOT:PSS surface at 3000 rpm for 60 s and baking at 100°C for 30 min under vacuum protection. Quantum dots were also deposited on the annealed poly-TPD surface by spin coating at 3000 rpm for 30 s. Then the synthesized ZnO nanoparticle solution was spin-coated at 1500 rpm for 60 s. The baking temperature is 60°C for 30 min. The cathode was deposited by vapor deposition method.

A more detailed QLED device fabrication process was mentioned in previous work [2].

### 3.4 Results and discussion

#### 3.4.1 ZnO nanoparticle analysis

The concentration of precursor, evaporation rate, and the time of reaction were all significant synthetic parameters, which affected the growth of ZnO nanoparticle dimensions and structures. Figure 5 shows the TEM images of the as-synthesized

![Figure 5](image-url)

**Figure 5.**

TEM images of two different sizes of ZnO NPs. (a, b) reaction times of 105 min and (c, d) 80 min.
ZnO NPs from a well-dispersed ZnO colloidal solution carried out with the reference condition. To investigate the effect of reaction time on the growth morphology, reaction times of 80 and 105 min were carried out. The nanoparticle’s size is smaller in the reaction of 105 min than in the reaction of 80 min. Moreover, the crystal lattice fringes are more clearly observed in the 105 min reaction sample rather than in the 80 min reaction sample. According to confinement effect, particles with smaller diameter would have higher energy. Therefore, the ZnO NPs used for QLED preparation are the smaller ZnO NPs.

In order to analyze the bandgap and quantum effects of the different ZnO NPs, their absorption and photoluminescence spectra need to be measured, which will be processed in future study. The energy bandgap (Eg) of the colloidal ZnO nanoparticles is determined from the intercept between the wavelength axis and the tangent to the linear section of the absorption band edge. The energy bandgap of ZnO NPs at 2.9 nm is 3.65 eV. The energy bandgap for the 5.5 nm ZnO NPs was 3.35 eV [17], while the energy bandgap of bulk ZnO is 3.2–3.3 eV [18], which is lower than the energy bandgap of ZnO NPs. It is found that the tendency of energy bandgap enlargement with decreasing size is consistent with the relationship based on effective mass approximation. Therefore, the reaction of 105 min can obtain smaller ZnO NPs than the ZnO NPs in the reaction of 80 min. In addition, the lattice fringes can be clearly observed in the TEM images, which suggests good crystallinity of the ZnO NPs.

3.4.2 QLED device performance and analysis

Figure 6(a) shows the structure of the QLED device, while Figure 6(b) shows the energy band diagram of the QLED device. The QLED device is a multilayer structure, which consists of PEDOT:PSS, poly-TPD, QDs, ZnO NPs, and Al. The thickness of each layer was measured by the surface profile (Alpha-Step 200 Tencor). Figure 7 shows the TEM image of quantum dots; the diameter of the quantum dots was around 7 nm.
The energy-level diagram in Figure 6(b) illustrated that the electrons and holes can be easily recombined together in the emission layer. Because ZnO NPs have a wide energy bandgap, the holes can be stored in the quantum dot layer. At the same time, poly-TPD’s energy bandgap is from $-2.3 \text{ eV}$ to $-5.4 \text{ eV}$. $-2.3 \text{ eV}$ is larger than $-3.8 \text{ eV}$, which can also restrict electrons in the quantum dot layer. What is more, adding PEDOT: PSS layer and poly-TPD layer reduces the energy gap for holes jumping into the emission layer (quantum dot layer). The introduction of ZnO NPs has a similar function as PEDOT:PSS and poly-TPD, which confine the excitation and recombination region, hence potentially improving the efficiency of photon generation. The thin layer structure of QLED device makes it a promising candidate for the next generation of flexible displays.

Figure 8 shows the device performance analysis. The turn-on voltage is shown in Figure 8(a), which is between 2 V and 3 V. The low turn-on voltage is due to the high electron mobility of the ZnO NPs and the design of the QLED structures. When there is a current applied to the device, the electrons can easily be injected into the emission layer, while the holes can also flow to the emission layer easily and be restricted by the ZnO NP layer. At the same time, the electrons accumulate at the interface of the poly-TPD/quantum dots due to the $-1.5 \text{ eV}$ energy offset between the LUMO of poly-TPD and quantum dots. When one high-energy hole can be obtained after absorbing the energy released from the interfacial recombination of an electron/hole pair, the high-energy holes can cross the injection barrier at the poly-TPD interface and recombine with the electrons inside the QD layer and then emit photons. This is called the Auger-assisted hole injection [14, 19]. Therefore, the high electron mobility of ZnO nanoparticles and the band alignment structure can facilitate the hole transport and balance of the carrier injection of the device.

The electroluminescence (EL) spectra of the QLED under different voltages are shown in Figure 8(b). The inserted picture is the QLED device. The EL intensity of the QLED device increases as the applied voltage increases. The wavelength is 534 nm with the
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full width at half maximum (FWHM) value is 44 nm through the spectrum. The peak wavelength of QLED electroluminance spectra is 2 nm red shift compared with the peak wavelength of QD solution, which might be because of the dot-to-dot interactions in the close-packed solid film. Moreover, the electric field induced the Stark effect [20]. The 1931 CIE coordinate after emission is (0.31, 0.66) as shown in Figure 8(c).
4. Conclusions

This work discussed the structure and mechanism of QLED and demonstrated an all-solution process of QLED in the last section. The QLED has high luminance with low turn-on voltage. These properties, caused by the use of ZnO NPs, improve electron injection and enhance radiative recombination. The resulting QLED fabrication process also makes printing QLED a possible method in the future.

Conflict of interest

The authors declare no conflict of interest.

Nomenclature

QLED quantum dot light-emitting diode
QD quantum dot
DOD drop on demand
HDTV high-definition television
CRT cathode-ray tube
LCD liquid crystal display
LED light-emitting diode
OLED organic light-emitting diode
PEDOT:PSS poly(ethylenedioxythiophene):polystyrene sulphonate
ZnO NPs zinc oxide nanoparticles
ITO indium tin oxide
Poly-TPD poly(N,N′-bis-4-butylphenyl-N,N′-bisphenyl)benzidine
EGBE ethylene glycol butyl ether
ODA octadecylamine
TOPO trioctylphosphine oxide
DMSO dimethyl sulfoxide
HTL hole transport layer
HIL hole injection layer
EIL electron injection layer
ETL electron transport layer
EML emission layer
HOMO highest occupied molecular orbital
LUMO lowest unoccupied molecular orbital
λ wavelength
h Planck’s constant $h = 6.63 \times 10^{-34}$ Js
P particle momentum
E the energy of a single particle in free space
m mass of a single particle in free space
ν the velocity of a single particle in free space
k the magnitude of the wave vector
L standing wave/the diameter of QDs
J current density
μ carrier mobility of materials
V voltage
ε dielectric constant
d the thickness of the thin film
FWHM full width at half maximum
Author details

Ning Tu
Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Kowloon, Hong Kong

*Address all correspondence to: ntu@connect.ust.hk; ningtu91@gmail.com

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