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Quantum Dot-Based Light Emitting Diodes (QDLEDs): New Progress

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Abstract

In recent years, the display industry has progressed rapidly. One of the most important developments is the ability to build flexible, transparent and very thin displays by organic light emitting diode (OLED). Researchers working on this field try to improve this area more and more. It is shown that quantum dot (QD) can be helpful in this approach. In this chapter, writers try to consider all the studies performed in recent years about quantum dot-based light emitting diodes (QDLEDs) and conclude how this nanoparticle can improve performance of QDLEDs. In fact, the existence of quantum dots in QDLEDs can cause an excellent improvement in their efficiency and lifetime resulted from using improved active layer by colloidal nanocrystals. Finally, the recent progresses on the quantum dot-based light emitting diodes are reviewed in this chapter, and an important outlook into challenges ahead is prepared.

Keywords: quantum dot, organic light emitting diode, efficiency, lifetime, active layer

1. Introduction

Due to increased population and consumption of more energy, the people of Earth are faced with a serious shortage of energy resources. Therefore, the primary concern of researchers and manufacturers is closely linked to energy consumption. In recent years, a lot of researches are conducted to achieve efficient and low-energy light sources. Inorganic light emitting diode (LED) and organic light emitting diode (OLED) have been introduced as a result of these efforts to achieve solid-state light sources [1–6]. The outdoor application is one of the important markets for LED lighting. For year 2015, the assessment of the total outdoor lighting market was \$6.5 billion USD with LEDs. The outdoor lighting market is expected to grow with

growth rate about 4% from 2015 to 2021 [7]. LEDs were used in many applications such as television backlight units and illuminated signs. The US Department of Energy has reported that the achievements to the expected developments in LED technology would save 300 TW per hour of electricity [8]. It means that a remarkable strategy needs to be developed for the simple design and better material to reduce the cost of fabrication. According to Stephanie Pruitt report, the packaged LED profits hit 15.4 billion dollars in 2014 and will grow to 22.1 billion dollars in 2019 [9].

2. Why OLEDs?

In recent years, the display industry and lighting panels have been changed. Many researchers are interested in using polymers and organic molecules as emissive layers in these devices to improve their characteristics. One of the most important developments related to OLED technology provides the ability to build flexible (can be deposited onto substrate like plastic), transparent and very thin displays and components. Simply an organic light emitting diode is constructed with a thin film of organic (carbon-based) put between a conductive cathode (electron injection site) and a conductive anode (electron removal site) considering that at least one of the electrodes should be transparent. This thin film is called emitter, which is electroluminescent; it emits light when excited by an electrical current. These organic matters have conductivity levels between insulating and conductive; therefore, they are considered as organic semiconductors. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in organic semiconductors are similar to the conduction and valence bands in inorganic semiconductors. The performance of OLEDs reaches important goals in display technology. In addition, OLEDs have many advantages over both LCDs and LEDs such as thinner, lighter, more flexible and brighter substrate. Moreover, OLEDs unlike the LCDs do not need a backlight and filters; thus, they are very thin, and their construction will be easier and reliable. Due to low energy consumption, OLEDs will be an important advantage for cellphones, which are battery-operated devices. Another important feature of the OLED is the solution-based emitting materials used in their structure. It can be possible to fabricate them into large area by a spin-coating method, which is low-cost fabrication techniques [10]. Also, OLEDs can be produced into large, thin sheet which makes them an interesting choice for industry. In addition, changing information in this technology is in real time, which is faster than LCDs.

The ability of a light source to reveal the colours of objects compared to a natural light source is called colour rendering index (CRI). This parameter is the most important advantage of an OLED in comparison with LED. Consequently, OLEDs have attracted a lot of attention due to light weight and high image quality. These features lead to a wide range of applications in industry, particularly in manufacturing flexible screens and full-colour light emitting pages. But there are still some problems like sensitivity to water vapour. Also, the production costs should be reduced more. Technology of OLED has much room for continuous progress in future. On the other hand, the fabrication process of small-molecule OLEDs is too expensive because thermal deposition with high vacuum is required. However, polymer-based OLEDs (POLEDs) are

the good substitute due to their solution process, which makes them more cost-effective. In fact, straightforward way of fabrication is the necessary factor for the low-cost electronic devices. Another advantage of POLEDs is their lower power consumption in comparison with traditional option. Therefore, many researchers are interested in developing POLED technology. Bottom-emitting conventional, bottom-emitting inverted, top-emitting conventional and top-emitting inverted are the four different architectures of POLEDs. Bottom-emitting inverted and top-emitting inverted can increase operational lifetime and reduce the fabrication and operating cost of the device. In addition, top-emitting conventional and top-emitting inverted can increase light out-coupling efficiency.

3. A brief review of OLED development

The first OLED was manufactured in 1987 by Tong in Kodak company [11]. He realized when an electric current is applied to the molecules of the organic material, this material emits green light. This was the first idea about OLEDs. In the first OLED, the structure was built by an indium tin oxide (ITO)/aromatic diamine/8-hydroxyquinoline aluminium (Alq3)/Mg-Al metal electrode. Up to now, the most organic components used in OLEDs are poly(para-phenylenevinylene) (PPV) [12], polyvinylcarbazole (PVK) [13] and aluminium-tris-(8-hydroxyquinoline) (Alq3) [14, 15]. To commercialize the OLEDs, several aspects must be improved. Therefore, during two decades, a lot of efforts have been made to achieve high performance of OLED devices. For example, the ability of charge injection, charge transport and emission of different layers of OLEDs are three important factors in their performance. To improve these factors, much effort has been devoted by researchers. They have tried to find better anode and cathode materials. They have also attempted to synthesize new materials' high emissivity. Therefore, development in synthesis process and application of electron transport materials, modification of surface in hole injection layer and electron injection layer, using high mobility materials in hole and electron transport layer (ETL), doping the high efficiency emitter dopants in emission layers and reducing the barrier to charge carrier injection by increasing the doping level of materials, was received [16, 17].

To achieve high-brightness display, high electron mobility is necessary in electron transport materials. For enhancement of charge injection, scientists try to use different cathode, and simultaneously, they have tried different surface treatments of ITO [18]. It is well known that employing electroluminescence material with high mobility is required for low-power consumption. On the other hand, the voltage can be decreased by doping, but rapid dopant diffusion can create the quenching centres in the emissive layers, which result in reduction of efficiency. Balancing of electron and holes will increase the efficiency of device that can be achieved by controlling the mobility of the transport layers. Therefore, an increase in the exciton recombination probability and control of the carrier accumulation needs to be adjusted for improving the current and power efficiencies by aligning the bands at the interface between the emitting layer (EML) and ETL [19]. Water/oxygen permeability is another that factor must be noticed. Moreover, encapsulation with a barium oxide (BaO) or calcium oxide (CaO) is used in OLEDs, and an acceptable level of water/oxygen permeability is achieved [20]. As

mentioned above, the architecture of OLEDs is one of the parameters that need to improve the performance of organic light emitting diode. So far, different structures of the OLEDs are investigated. Scientists have tried to improve the performance and stability of these devices by substituting of alternative material in different layers of OLEDs. For example, carbon nanotubes [21, 22], graphene [23, 24], metal nanomeshes [25, 26], thin metal films [27, 28] and metal nanowires [29, 30] are employed instead of ITO up to now. In addition, Burns et al. have investigated the effect of thermal annealing super yellow emissive layer on efficiency of OLEDs [31]. By annealing of the emissive layer at 50°C, the external quantum efficiency (EQE) of this device reached a maximum of 4.09%.

4. Looking to the future: outlook

OLEDs have been commercialized in tablet, smart watches and smart phones up to now, and they are stable devices with good efficiency. But they still need to achieve more improvements. Higher efficiency, better stability and being more environmentally friendly are some important factors that researchers are trying to improve them. Samsung has manufactured its mobile displays by red, green and blue OLED subpixels, and LG used white emitting OLED material with WRGB colour filters for its TVs. OLED display includes red, green and blue pixels. The most critical issue is the blue gap in OLED materials. Nowadays, display industries use fluorescent materials for blue colour, but the use of fluorescent materials involves with an increase in power consumption. Therefore, new approaches should be introduced in the technology of the OLED display. From technological point of view, the fluorescence, phosphorescence and thermally activated delayed fluorescence (TADF) are three mechanisms to harvest excitons in OLEDs and considered for improvement of their performance. High-performance and low-cost OLEDs are available after discovery of metal-free organic emitters with thermally activated delayed fluorescence (TADF). There are two kinds of TADF emitters named organic and metal-organic. The maximum external quantum efficiency of these OLEDs has been reached to 25% up to now [32]. The efficiency of TADF OLEDs is comparable with phosphorescent OLEDs. The most value of TADF OLED lifetime is reported over 10,000 h. Carbazole [33, 34] or arylamine-type donors [35, 36] are the main organic TADF emitters that are reported up to date. The excited-state lifetime or emission decay time of materials is the important problem that should be solved to commercialize TADF OLEDs. It needs more developments in this field.

5. Structure of OLEDs

Structure of OLED is another factor that can be employed to improve its characteristics. At the device level, each OLED pixel is a p-n junction that emits lights. Top emitting and bottom emitting are two main configurations of the OLEDs. Up to now, top emitting is a common structure that has been used to increase efficiency and the light output of the device by the display industry. When the current source creates potential difference in OLED circuit, a variable

voltage between 2 and 10 V is applied between the cathode and the anode, and the flow of electrons from the cathode to the anode is established. After a while the negative charge density in the electron transport layer and the positive charge density in the hole transport layer will increase. Today, some thin layers are used between two conductive layers in order to achieve better performance of OLEDs. The half-life of the device can be reduced by high voltage. Therefore, highly conductive transmission layer is used to reduce injection barriers and achieve low-voltage operation in modern OLEDs. The basic and typical structure of an organic light emitting diode has been shown in **Figure 1**.

The anode is positive compared to the cathode, so the electrons flow from the cathode to the anode. The electrons injected into the cathode are placed in the LUMO level of the organic layer, and they also will withdraw in the HOMO level of the organic layer. Holes arrive from the hole transport layer to the HOMO level. The energy level of the emissive layer should be less than the hole transport layer in order that the injection of the electrons from electron transport layer to LUMO level of the emissive layer to be possible. To penetration the holes into emissive layer, this layer also should have higher HOMO level than HOMO level of the hole transport layer.

Electrostatic forces bring the electrons and holes towards each other and form the excitons in a singlet/triplet ratio of 1:3. It happens near the emissive layer. **Figure 2** shows the population of emitter states by energy transfer from singlet and triplet excitons. It is important to note that the holes are more mobile than electrons in organic semiconductors and arrive to electron transport layer faster. The destruction of this excited state led to radiation in the visible region. If the active layer is phosphorescent, non-radiative triplet excitons may be emitted. The frequency of this radiation depends on the difference between HOMO and LUMO levels of these materials. Because the holes must be logged in the HOMO level of the organic material in emissive layer with energy levels about 5–6 eV, anode with high work function is required till holes will be able to effectively enter to the organic material. Also anode should be transparent in order for the produced photons to be visible. ITO is often used as anode material because it is transparent compared to visible light. In addition, the injection of holes into the HOMO level of the organic layer will be possible due to its high work function.

Figure 1. The structure of (a) basic and (b) typical organic light emitting diode.

Figure 2. Population of emitter states by energy transfer from singlet and triplet excitons.

To inject electrons into the LUMO level of the organic layer, the work function of the cathode should be low. Calcium and magnesium are two metals used as cathode due to their low work function. But the drawback is that these metals are sensitive to moisture and therefore will reduce the lifetime of the device. To solve this problem, aluminium or various alloys such as Mg/Ag as a cathode are used as cathode [37–39]. **Figure 3** shows the evolution of OLED device structure. The electron and hole transport layers could help to high-speed movement of electrons and holes to meet each other in the emission layer. Electron transport layer prevents the penetration of hole into cathode, and in contrast hole transport layer prevents the penetration of electrons to the anode. The electrons and holes recombine with each other in

Figure 3. Evolution of OLED device structure.

the middle of emissive layer. The material of the hole transport and the electron transport layers (electron and hole blocking layers) depends on the characteristics of the charge and the values of the HOMO and LUMO levels. Usually PEDOT:PSS is used as a conductive layer in which its HOMO level is between the work function of the ITO and HOMO level of the commonly used polymers in order to reduce the energy barrier of the injecting holes.

6. Different types of the OLEDs

To date, various types of the organic light emitting diodes are presented. The six main types of the OLEDs are passive-matrix OLED (PMOLED), active-matrix OLED (AMOLED), transparent OLED, top-emitting OLED, foldable OLED and white OLED. Each of these types has different kinds of use. PMOLED consists of cathode, organic layers and anode. The manufacture of this type of OLED is easy. They have high-power consumption; therefore, they are effective for small screens. Passive-matrix addressed displays are attractive, as the device construction is relatively simple. AMOLED is composed of cathode, organic molecules and anode layers. The anode layer is established on a thin film transistor (TFT) and formed a matrix. Because of the use of less power, they are suitable for large-sized displays. Substrate, cathode and anode are transparent in the transparent OLED. Top emitting OLED consists of an opacity substrate, and it is suitable for active-matrix design. Foldable OLED has a flexible substrate made of metal or plastic that is very lightweight and durable and can be used in clothes with OLED display. White OLED emits white light that is brighter, more uniform and more efficient than fluorescent lights.

7. Important features of OLEDs

Quantum yields and lifetime are the two important characteristics of an OLED that researchers are trying to improve by different structures and techniques all around the world. Optimizing the balanced charge is an important issue for the lifetime of the device. Also choosing the right ingredients in the manufacture of layers can be useful in improving the performance of the device. OLEDs have the limited peak emission so that the highest peak luminance of OLEDs is at most 500–600 nits. But this value for LCD TVs is about 1800 nits. The amount of the light emitted divided by the amount of the injected current into the piece is called quantum yields of an OLED. High yield achievement and suitable coordinates of colour for display applications are the other important features of an OLED. External quantum efficiency (EQE) can be explained in following formula:

$$\text{External quantum efficiency } (\eta_{\text{EQE}}) = \gamma \chi \cdot \eta_{\text{PL}} \eta_{\text{OC}} \quad (1)$$

γ = recombination efficiency of holes and electrons; χ = fraction of excitons with spin allowed optical transitions, created in emissive layer; η_{PL} = photoluminescent efficiency of the emitter; η_{OC} = fraction of emitted photons that are coupled out of the device ($1/2n^2$); n = refractive index of the substrate (glass).

Electrons and holes which meet each other in active layer create different states; about 25% of the excitons are in the singlet states, and the rest of them are in the triplet states. Therefore, the maximum internal efficiency of the OLEDs based on fluorescent molecules is around 25%. It can be possible to improve the efficiency of OLEDs by enhancing spin-orbit coupling and enable emission from the formally forbidden triplet state with the use of phosphors. Totally, display devices are typically assessed through a number of characterization measurements that include colour coordinates (perceived colour), current density (A/cm) versus voltage, luminance (a measure of brightness in cd/m^2) versus voltage, current efficiency (cd/A) versus luminance, power efficiency (lm/W) versus luminance and lifetime (a measure of the stability of the device). Kim and his colleagues in 2014 have shown that approximately 35.6% EQE can be reached by using iridium compounds (HICs). This efficiency is one of the highest external quantum efficiencies achieved to date in the red OLEDs [40]. OLED has already been commercialized; LG company has commercialized the OLED-based TVs. OLEDs are emissive displays, which means they create their own light at each pixel, like CRTs and PDPs. But as mentioned, the possibility of degradation in the presence of moisture and oxygen is the big problem needed to be considered. There are several damaging processes in these materials such as thermal instability, optical and chemical oxidation of the active layer and penetration of the metal from electrodes [41]. So it should be a process for encapsulating structure to protect it from the influence of moisture and oxygen. Also, by replacing the organic materials to inorganic structures, there will be the possibility of a better stability. The best results have been achieved up to date related on the usage of quantum dots based on cadmium. Employing nanoparticles such as oxides and semiconductors to form composite materials is one of the available solutions to improve the stability of these devices [42]. Not only adding nanoparticle can increase the stability of the film, but also it will be possible to control the optical properties by adjusting their size. Thus this would be an appropriate way for optoelectronic applications. For example, the gap between energy levels (luminescence colour) of semiconductor increases by reducing the particle size.

8. A brief review of quantum dot-based light emitting diodes (QDLEDs)

Being cost-effective, much more brightness and more efficient as well as more stable devices made of environmentally sustainable materials are the most important factors that led to the development of the lighting industry. A new candidate for improvement of display industry is emissive layer based on quantum dots (QDs). Quantum dot technology is a novel innovation to help this industry. This technology has also applications in many other markets such as solar cells, biomedical, instrumentation, quantum computers and more. Quantum dot technology seems to offer the biggest colour gamut of the various approaches today. Quantum dots have three key elements to their structure. Core, shell and ligand are the three main properties of the structure of the QDs. The core adsorbs and re-emits the light. The shell layer is responsible to confine the emission and passivate defects in the structure. The ligand layer provides more stability. The addition of barrier layers is required to protect QDs from

oxygen, water and heat. Quantum dot-based light emitting diodes (QDLEDs) are a new form of light emitting technology based on nanoparticle, and their structures are similar to the OLED technology. Although, in this technology, a layer of quantum dots is placed between electron and hole-transporting layers, like sandwiched structure. Electrons and holes are accumulated in the quantum dot layer by an applied electric field. Then, they will recombine and emit narrow spectrum of photons. For example, FWHM for Cd based is 25–35 nm and 40–50 nm for Cd-free QDs.

The efficiency of QDLEDs is still lower than OLEDs. But the pure emission colour, the easier tenability of colour emission by adjusting the particle size and their lower emitter cost make them interesting subject for researchers as well as artisans. Conducted researches improve the quantum efficiency of QDLEDs more than two order of magnitude up to now. A bounded electron and hole inside the QD can recombine and emit a photon that has energy equal to the gap between the highest occupied and lowest unoccupied states. In 1994, the first structure of organic light emitting diodes based on quantum dots is studied. This structure consists of a layer of CdSe quantum dots and the polymeric electron transport layer, which are placed between two electrodes [43]. Due to low mobility of organic semiconductor, QDLED had low performance, and the threshold voltage was as large as 4 V. Recently, a new colloidal quantum dot-based light emitting diode (QDLED) is reported with improved external quantum efficiencies (EQE) by applying the organic CIM/LiF/Al cathode [44]. QLEDs with this new structure increase the EQE about 25% comparing to the bare Al devices. Therefore, using an organic cathode interfacial material can result in better device performance, including the brightness, EQE and CE. In this proposed device, the peaks of EQE and CE were 8.5% and over 29 cd/A, respectively. This improvement is because of balanced electron/hole injection due to the presence of the organic CIM. The balancing of the carriers is hard, because most quantum dots are considered in n-type materials. So the current efficiency will be low in these devices. The p-type conductivity and hole injection barriers of the organic hole transport layer are necessary to improve the efficiency of QDLEDs. Further attempts are aimed to optimize charge injection, to transport, to improve stability of material and to control chemical and physical phenomena at the interface. Also, an all solution-processed QDLED with an inverted structure is investigated by Castan and his coworkers [45]. They demonstrated that the optimized amount of PTE in the PEDOT:PSS can balance the charge in the device. The red, green and blue devices using this structure have maximum luminance about 12.510, 32.370 and 249 cd/m² and turn-on voltages of 2.8, 3.6 and 3.6 V, respectively. Because of the process used for the fabrication of this device, it is very promising in the future of display industry.

In addition, highly bright and efficient blue QDLEDs have been reported by employing ZnCdSe core/multishell QDs as emitters [46]. The efficiency and brightness were improved by doping poly vinyl(N-carbazole) (PVK) in the emissive layer. It balances the charge injection because of the lower HOMO level, which causes the reduction of potential barrier at the interface of QDs and hole transport layer. This blue QDLEDs show a high efficiency (EQE > 8%), and the peak of efficiency happens at the luminance about 1000 cd/m². In 2007, Xie et al. found that the inorganic core oxidizes through their lifetime. So they suggested growing the

shell materials on the surface of the core to passivate the inorganic core [47, 48]. They could improve stability by growing a ZnS shell around the InP core. The properties of QDs strongly depend on their shell and their compounds. The cluster diameter is a significant factor in determination of bandgap in structure of the QDs. The emission band will be narrower, while the diameter of the cluster gets smaller. Also the thickness of shell is important in increasing the maximum amount of the PL efficiency. According to the result of Bera and his colleagues' research, the thicker shell layer, the lower amount of photoluminescence quantum yield (PLQY) [49]. The main reason of this phenomenon is that the misfit dislocations (sites of non-radiative recombination) are formed when the shell layer is thick. Higher quantum efficiency will be available by minimizing these sites in QDs. In addition, matching the energy levels of the shell and core should be considered. Confining the excitons within the QDs is possible by selecting proper material of shell with wider bandgap to create an appropriate potential barrier around the QD.

Colloidal CdSe/ZnS (core-shell QDs) have high quantum yield and high photo stability at room temperature. So they are good choice in lighting industry, and many researchers have investigated them [50]. To prevent the light scattering, the particle size should be smaller than one-tenth of the visible light's wavelength [51]. On the other hand, large particles tend to accumulate that tarnish the composite film. The fluorescence properties of the QDs can be affected by the ability of QDs to aggregation. Accumulation effect can drastically reduce the quantum efficiency. Recent researches have demonstrated that the repulsive force between the molecular chains of polymers can prevent the accumulation of nanoparticles, so the compound of the polymer quantum dot can improve this problem. Up to now colloidal nanoparticles of cadmium sulphides, cadmium silicon and lead sulphides are used in organic light emitting diodes. These QDLEDs emit green light potentially [52–56]. On the other hand, these kinds of QDs have toxicological properties so it is environmentally restricted and not to be able to be a commercial material in this field. New Cd-free quantum dots should be introduced to commercialize the QDLED technology. ZnO cores with a MgO shell, InP-based dots and CuInS₂ are three new materials that need more studies to be performed by scientists [57, 58]. In 2015, Du et al. studied a stable photoluminescence QDLEDs based on hydrophilic CdTe QD. Inorganic nanocomposite CdTe quantum dots were prepared with two rotary steam and freeze-drying methods. Because of adhesion, flexibility and transparency, silica gel can be coated on the surface of UV light emitting diode and form photoluminescence QDLEDs. This new photoluminescence QDLED is sustainable and cost-effective. Also it is easy to operate and environmentally non-toxic [59]. Recently, Kim' group has studied a multiple structure of QDLED based on InP quantum dots. Current efficiency and brightness in this structure are reported to be 1 cd/A and 530 cd/m², respectively. As mentioned, the best results in improving the stability of organic light emitting diodes are based on Cd QDs. InP quantum dots are replaced with Cd QDs in this study because of the environmental risks of cadmium [60]. In addition, the interface trap states are very effective on the performance of the device. In 2016, Koh et al. investigated these traps in the presence of TCNQ between charge transfer layer and quantum dots. With the introduction of TCNQ, the electroluminescent efficiency (EL) in QDLED has been improved by increasing the charge injection into the QD layer [61].

ZnO nanowires are perfect single crystals, which increases the mean free path of carriers transmitted on them. High density of QDs layers is prepared by ZnO nanowires which caused much more brightness of QDLEDs. These ZnO nanorods allow high density for QD and provide brighter LED-based display. This structure emits light that is very similar to the sun's light, and energy transfer efficiency of this structure is measured and equal to 17% [62]. The efficiencies equal to 10.7 and 14.5% are obtained by combining electron transfer layer and hole transfer layer and using the Cd QD for blue and green QDLED, respectively. However, the efficiency of red QDLED has reached to 20% [63]. Furthermore, the red QDLED with reverse multiple structures and excellent performance with an external quantum efficiency of 18% has been reported [64]. Up to now the external quantum efficiencies of QDLEDs based on Cd QD obtained are 10.7% [65] and 14.5% [66] for blue and green QDLEDs, respectively, while red QDLED efficiency is 20.5% [67]. Of course, the higher efficiencies are obtained in OLEDs without the use of quantum dots. In many applications, nanoparticles are imported into the polymer to give a special feature. For example, nanoparticles improve stability of the host material, because they act as energy absorbers to reduce the structural defects of organic materials. The benefits of using nanoparticles are high stability, narrow emission spectrum and feasible use in the polymer structure and the formation of thin film layers. Dark details, image sticking, peak luminance, colour gamut, colour volume, efficiency and lifetime of QDLEDs are so much better than OLEDs. However, black level, haloing, viewing angle and being eco-friendly are the advantages of OLEDs comparing to QDLEDs. QDLEDs are the energy efficient and have tuneable colour display. They deliver about 35% more luminous efficiency in comparison with OLEDs at the same colour point. Also, power efficiency of QDLEDs can be twice more than OLEDs at the same colour purity. The last but not least advantage of QDLEDs over OLEDs is low-cost manufacture. They can be printed in large area on thin flexible substrates, and they are also solution processable [68]. QDs have very narrow emission spectra, but their absorption spectra are broad. Factually, they absorb all wavelengths higher than their bandgap and convert them into a single colour. This narrow spectrum will improve colour saturation in QDLEDs compared to OLEDs. In addition, QDLEDs can be more power efficient due to good colour coordinate and luminous efficiency.

QDs can be used in solar cells as well as LEDs due to their broad excitation band and narrow emission spectra. The tunable colour of QDLEDs will be provided by controlling the quantum dot size [69]. For example, cadmium selenide quantum dots can emit optical wavelength in the range of 470–640 nm by varying the size of 2–8 nanometres. The size of the QD can make unique physical properties in QDLEDs because the electrons in a nanocrystal exhibit quantum mechanical effects. The quantum confinement phenomenon occurred in nanocrystal will lead to discrete energy levels. The bandgap energy of a QD is inversely proportional to its size; therefore the emission from a QD will be colour tuneable. At present, the best OLEDs can have a quantum efficiency of up to 33%, which is much higher than that of QDLEDs [70]. Defects in the crystal create some non-radiative electron-hole recombinations that are the main reason of the low quantum efficiency. Although, the PL efficiencies of QDs are high, still the EQEs in these devices are low mainly due to poor charge carrier injection into the QD layers [71]. QDLEDs will be a good choice for the future of LEDs due to their

colour stability, easily tunable colour and long lifetime. In recent years, due to all the advantages of the QDLEDs mentioned above, many research groups have worked on QDLEDs [72–75], and the efficiency of this type of light emitting diodes has improved in subsequent researches [76–80].

9. Features of QDLEDs

QDLEDs are characterized by their total width at half maximum (FWHM). Moreover, having a high quantum yield and high charge transfer coefficient are two important features of the emissive layer [81]. FWHM is examined in these devices, and entirely these structures have a small FWHM. This value of a single QD size should be very small. However, the extension of the FWHM is unavoidable because there will be different sizes of the QDs. Because the size of the nanoparticles determines the wavelength of radiation and particles with similar size will be commensurate with the radiation intensity, radiation spectrum shows QD size distribution directly [82]. As mentioned above, the increase in FWHM shows that there is more diversity of QDs that can be caused by the reformation of QD result in exposure to UV and heat. When photons of UV are absorbed by colloidal quantum dots, the heat caused by losses stoke remains near to QDs and resizes QDs. Changes of FWHM will be more in higher currents. The use of semiconductor nanoparticles with narrow size distribution and narrow-band radiation leads to emit white light with low CRI. And this is because the CRI depends on the size and distribution of colloidal nanoparticles. In this way, we have developed a procedure for preparation of CdS colloidal nanocrystals. The emission spectrum of synthesized sample was shown in **Figure 4**. As can be found from this figure, FWHM of emission spectrum is reduced

Figure 4. Emission spectrum of CdS colloidal sample.

to 10 nm, which is very small [83]. The prepared sample displays a strong and narrow green emission peak centred at 519 nm that has not been reported before, and it is longer than the onset of absorption of ~512 nm for bulk CdS. Several weak emission peaks appeared at wavelengths 490, 506, 521 and 543 nm, too. These two important characteristics of the prepared sample are due to the strong band-edge emission of CdS nanocrystals. **Figure 4** shows the PL spectrum of CdS nanoparticles excited by wavelength of 190 nm.

10. Different types of QDLEDs

QDs are applied in three types of OLEDs. PLEDs which their emissive layer is based on polymers, fluorescent small molecules and PHOLEDs which are the organo-metallic phosphorescent small molecules. Phase separation and contact printing are two major fabrication techniques for manufacturing of QDLED. **Table 1** shows common materials and QDs used in QDLEDs and OLEDs. Emission wavelength of QDs can be controlled by its size or composition.

QDs are very impressed by the environment (humidity and oxygen), because of the small size of the QDs. As can found from **Table 1**, ZnO is one of the semiconductors that can be used as electron transport material. Recently, we have developed a procedure for preparation of high mobility nanostructured thin indium-doped ZnO film [84, 85]. **Figure 5(a)** shows the scanning electron microscopy (SEM) of nanostructured thin ZnO film, and the X-ray diffraction (XRD) has been depicted in **Figure 5(b)**. It can be seen that there are three sharp diffraction peaks approximately at 30°, 33° and 35° that correspond to (1 0 0), (1 0 1) and (0 0 2).

Materials	HOMO	LUMO
PEDOT:PSS	-5.4	-2.4
MoO ₃	-9.5	-6.5
a-NPB	-5.5	-2.4
ZnO	-7.5	-4
TPBI	-6.3	-2.8
TAZ	-6.4	-2.8
p-NiO	-5.4	-1.8
CdSe/ZnS (green QD)	-6.8	-4.3
CdSe/ZnS (red QD)	-6.7	-4.7
InP/ZnS (QD)	-5.2	-2.2

Table 1. Energy levels of some common hole and electron transport materials used in OLEDs and typical QDs.

Figure 5. (a) A scanning electron microscopy (SEM) image and (b) the X-ray diffraction (XRD) pattern of QD.

11. Conclusions and challenge ahead

It is expected to see much more progresses in the lighting industry particularly QDLEDs in the near future. Optimizing the efficiency of devices can help to improve the performance of QDLEDs. Many researchers try to do their best in this respect such as Shen and his group [86]. They have suggested a new high efficiency QDLED. Anikeeva et al. try to increase efficiency by using materials with high PLs in the red, green and blue regions of the visible spectrum [87]. Despite all efforts they made, improving the efficiency of blue QDLEDs seems to be challenging because of that the blue QDs and used electron and hole-transporting materials have low spectral overlap with each other. They expect that using wide bandgap hole and electron transporting organic materials improves the efficiency of the blue QDLEDs due to better exciton energy transfer and direct charge injection into the blue QDs. Hybrid devices that incorporate emissive layers using different types of emissive materials can play a big role in the future of QDLEDs. They could be made by a blue emitting TADF layer, a green phosphorescent layer and a red QD layer.

In conclusion, to improve the performance of the QDLEDs:

- 1. Improve the structure of QDLEDs.
- 2. Improve manufacturing techniques.
- 3. Choose a suitable material for the injection and transfer layers.
- 4. Structural differences of quantum dots.

There are a number of requirements that must be met in order for quantum dots to be integrated into the LED device and replace phosphor-based solutions. For one, the quantum dots should be stable in air, and moisture and the colour performance must be stable. Another problem faced to the development of the quantum dot materials is self-quenching. The quantum dots are designed to absorb light in one wavelength range and re-emit in another. The efforts of the researchers to create such a display are still in progress. QDLEDs promise to introduce very high contrast device, but with lower power than other technologies existed up to now. In addition, the lifetime of QDLEDs is another feature that needs more attention.

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