INVESTIGATING THE EFFECTS OF SOLVENT AND CONCENTRATION OF ZnO NANOPARTICLES ON THE PROPERTIES OF GREEN-QDLEDS FOR DISPLAY APPLICATIONS

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Abstract

Colloidal quantum-dot-based green light-emitting diodes (QD-LEDs) are attractive for use in display devices because of the remarkable electrical and optical characteristics of quantum dot materials. In this study, ZnO NPs were synthesized as the carrier transporting layer using a solution-mediated process. After that, all solution- multilayer QD-LEDs with a structure of ITO-Glass/PEDOT:PSS/PVK/Green-QDs/ZnO/Al/Encap was fabricated. The effect of the solvent on the emission layer was investigated, along with the effect of the ZnO NPs concentration of the electron transfer layer. The regular green-QDLED device showed a maximum luminance of 9865 cd/m^2, a luminance efficiency of 13.84 cd/A, and an EQE of 3.68%, at a turn-on voltage at 6.0 V.

Keywords: *Quantum dots materials; quantum dot-light emitting diode (QDLEDs); ZnO nanoparticles.*

1. Introduction

Quantum dots are nanoscale semiconductor particles with dimensions typically on the order of a few nanometers. They are predominantly fabricated using materials such as cadmium selenide (CdSe), lead sulfide (PbS), or indium phosphide (InP), although other materials can also be employed [1]. The intriguing properties of quantum dots emerge from quantum confinement effects, which manifest when the dimensions of the material become comparable to or smaller than the characteristic wavelength of the involved electrons or photons. These confinement effects give rise to size-dependent optical and electronic characteristics in quantum dots, enabling tunable light emission and absorption. A distinctive attribute of quantum dots is their size-dependent fluorescence or quantum

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confinement effect, whereby they emit light of different colors based on their size. This tunability of emitted light spans a wide spectral range, encompassing ultraviolet (UV) to near-infrared (NIR) wavelengths [2]. Consequently, quantum dot materials find applications in diverse fields such as display technologies, lighting, biological imaging, and photovoltaics [3].

Quantum dot light-emitting diodes (QDLEDs) have garnered significant attention in recent years due to their unique properties and potential applications [4]. QDLEDs have demonstrated exceptional color purity, high brightness, and wide color gamut, making them attractive for display applications. They can be used in next-generation TVs, monitors, and mobile device screens, offering vibrant and energy-efficient displays with improved color accuracy. QDLEDs have the potential to revolutionize lighting technology by providing highly efficient and tunable light sources. They can enable the production of energy-efficient and long-lasting lighting solutions with customizable colors, leading to improved color rendering and enhanced visual experiences. Furthermore, QDLED technology has been leveraged in quantum dot TVs, also known as QLED TVs. These TVs utilize quantum dots as a color filter layer, allowing for a wider color gamut and enhanced color accuracy compared to conventional LCD displays. QLED TVs offer vivid and lifelike images with improved brightness and contrast ratios [1, 5].

The QDLED device structure consists of several layers, including the quantum dot layer, charge transport layers, and electrodes. The substrate is typically coated with a transparent conductive layer, such as indium tin oxide (ITO), which serves as the anode. Additional layers, such as hole transport and electron transport layers, are then deposited on top of the anode to facilitate charge injection and transport. There are several methods to make QDLEDs, however, spin coating known is a common method used to deposit layer by layer in the fabrication of multi-layer structure quantum dot light-emitting diodes. In this work, all solution process green-QDLEDs have a normal device structure of ITO-Glass/PEDOT:PSS/PVK/Green-QDs/ZnO/Al/Encap achieved a maximum luminance of 9865 cd/m^2, luminance efficiency of 13.84 cd/A and maximum EQE of 3.68%. To obtain these results, we solve the problem of solvent damaging the underlying layer by studying effects of toluene, n-hexane, and octane. Besides, the effect of ZnO nanoparticle concentration was investigated to optimize the QDLED device performance.

2. Experiment

2.1. Materials preparation

ZnO nanoparticles were synthesized following the procedure reported in previous reports [6, 7]. In this work, zinc acetate dihydrate (1.18 g) was poured into a three-neck flask with methanol (50 ml) and then stirred at 62ºC. A solution of KOH (0.592 g) in methanol (26 ml) was then dropwise in the flask at 65ºC over 15 min of a period. The reaction mixture was stirred for 2.5 h with vigorous stirring 1000 rpm. After cooling to room temperature, the supernatant was decanted and the precipitate was washed three times (3500 rpm, 3300 rpm, and 3200 rpm) with methanol (20 ml) using the centrifuge to get ZnO nanoparticles. A solution of n-Butanol (28 ml), methanol (2 ml), and chloroform (2 ml) was added to disperse the precipitate and produced a ZnO nanoparticle solution with a concentration of 6 mg/ml. After synthesis, the solution of ZnO nanoparticles was maintained in the refrigerator. The ZnO nanoparticle solution was ultrasonicated and filtered through a 0.45 µm PTFE-H syringe filter before making QDLED devices (Fig. 1).

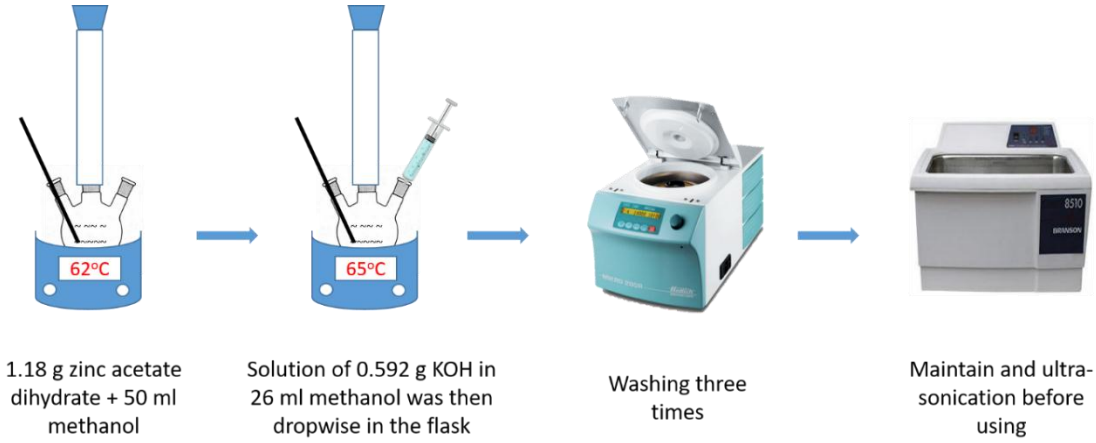


Fig. 1. ZnO synthesis process.

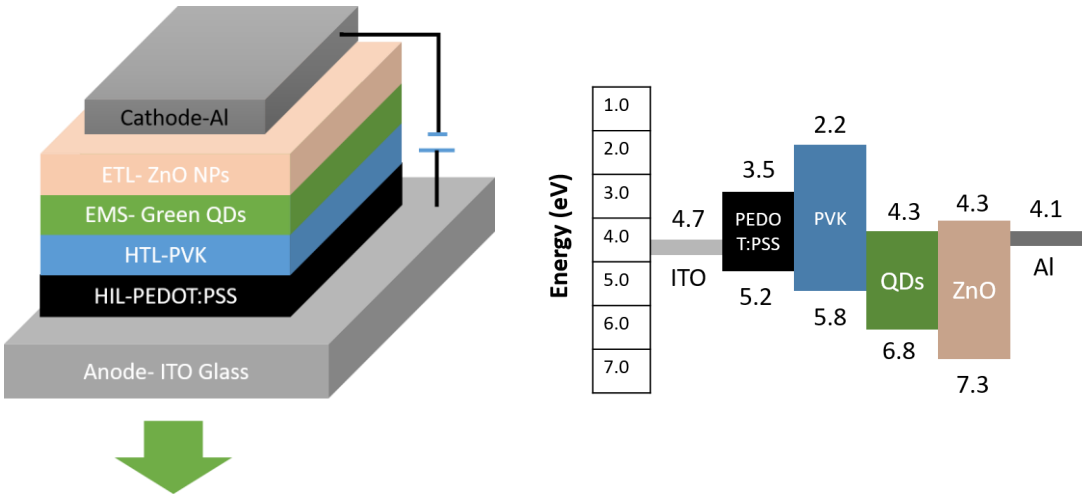
The colloidal Green CdSe/CdS/ZnS core/shell quantum dots (QDs- from Global ZEUS) was mixed in various solvents to get the concentration of 10 $mg.ml^{-1}$. With the same concentration of QD solution, Poly 9-vinylcarbazo (PVK- from Sigma-Aldrich) was dissolved in Chloroform and then stirred for 2 hours at 500 rpm and room temperature.

Highly conducting PEDOT:PSS (Clevios^{TM} PH1000) was purchased from Heraeus. The pristine PEDOT:PSS was filtered through a 0.45 µm ether-sulfone before spin-coating to make QDLED devices.

The Indium Tin Oxide patterns as the device substrates were prepared by photolithography technology.

2.2. Green-QDLED devices fabrication

Figure 2a shows the regular structure of the ITO/PEDOT:PSS/PVK/Green-QDs/ZnO/AL/Encap [8, 9]. All devices were fabricated on the ITO-glass (20 Ω.□$^{-1}$), which was sequentially cleaned by DI water, isopropanol alcohol, and acetone in an ultrasonic bath (20 min for each step). Then ITO glass substrates were treated for 30 min by UV-zone. In a conventional structure QDLEDs, a hole injection layer (HIL) of PEDOT:PSS (Clevios P VP AI 4083) was spin coated onto the cleaned substrate at 3500 rpm for 60 s and followed by annealing at 150°C for 30 min. Thereafter a hole transport layer (HTL) of Poly(N-vinylcarbazole) (PVK, 10 mg/ml in chlorobenzene) was spin-coated onto the PEDOT:PSS coated ITO-glass with the same spinning and baking conditions as above. The QD patterns were sprayed by EHD jet printing with various parameters and types of spraying methods, and then dried at room temperature for 10 min. Afterward, a ZnO solution as an ETL was deposited by spin coater at 2500 rpm for 35 s, followed by baking at 110°C for 30 min. Finally, a 100 nm thick aluminum was thermally evaporated on top of the ETL at 1.2 × 10^{-6} Torr, thus completing the multi-structure of the QD-LEDs. To protect against moisture and oxygen, Green-QDLED devices were encapsulated by UV epoxy and transparent glass [6].



(a) *(b)*

Fig. 2. (a) Regular QDLEDs structure (b) The band gap energy diagram of the fabricated QD-LEDs.

The morphological layers were step-by-step carefully observed via a Nanoview System. The device characteristics, the electroluminescence (EL) spectra, the current-voltage-luminance (J-V-L), and the CIE color space were measured in a dark box using a Keithley 2400 SourceMeter connected with a SpectraScan PR 670 Spectroradiometer. All measurement was recorded under the ambient conditions.

3. Results and discussion

3.1. Effect of solvent in QDs for performance of QDLED devices

Figure 2b shows the energy bandgap diagram of conventional QDLED devices. In this structure, the electron is injected from Aluminum due to the LUMO of ZnO NPs 4.3 Ev, which is similar to the work function of Al, 4.1 Ev. The HOMO of ZnO is 7.3 eV, which is sufficiently large to block hole transport to the ETL. On the other hand, in this structure, PVK was inserted as a hole balance offset between the layers to improve hole transfer to the QDs. The energy level diagram shows that there is a large difference between the HOMO of PEDOT:PSS (5.2 eV) and Green-CdSe/CdS/ZnS QDs (6.8 eV). PVK with a HOMO of 5.8 eV was inserted to compensate for the energy difference and improve hole injection. The arrangement of HOMO and LUMO are convenient for hole to transport from the anode and combines with the electron from the cathode to emit the light in the QDs- EML layer [8, 9].

For the fabrication multilayer structure device, each layer should be carefully investigated for balance-electron injection. Using the spin-coating method, we investigate the effect of spin rate, and spin time to get good morphological surface of each layer. Besides, the compatibility between solvents in two closed layers is the point for the first studies. In this work, toluene, hexane, and octane were examined as a solvent for Green-QDs for preparing QDLEDs. The solvent of ELT layer (ZnO in the solution of n-Butanol: methanol: chloroform) also affects the QD layer, and the adhesion of QD layer to HTL-(PVK in Chloroform) underneath layer is also important. An interesting result was obtained. All solvents expert n-hexane showed poor luminescence with lower efficiency. Even though, n-hexane is a very quick evaporation solvent, it is hard to get a good morphological thin film via spin-coating. QDLED with QDs in hexane obtained the highest maximum luminance of 6448 cd/m^2 (Fig. 3). Devices with solvents of toluene and octane achieved maximum luminance of 3808 cd/m^2, and 5780 cd/m^2, respectively. Fig. 4a shows a real Green-QDLED device. Right side, Fig. 4b shows a very bright

luminance QDLED device that was captured during measurement. The optical and electrical properties of Green-QDLEDs with various solvents for QDs were also summarized in Table 1.

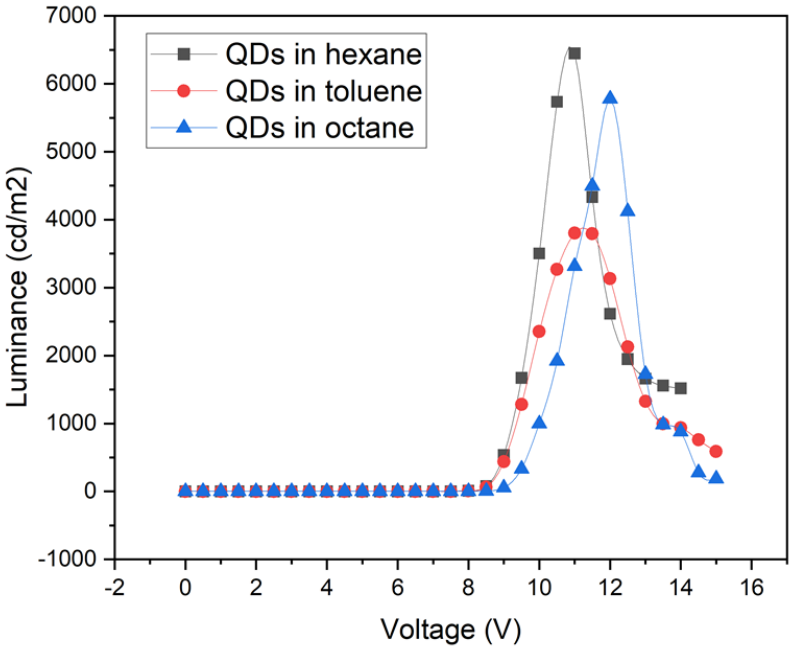
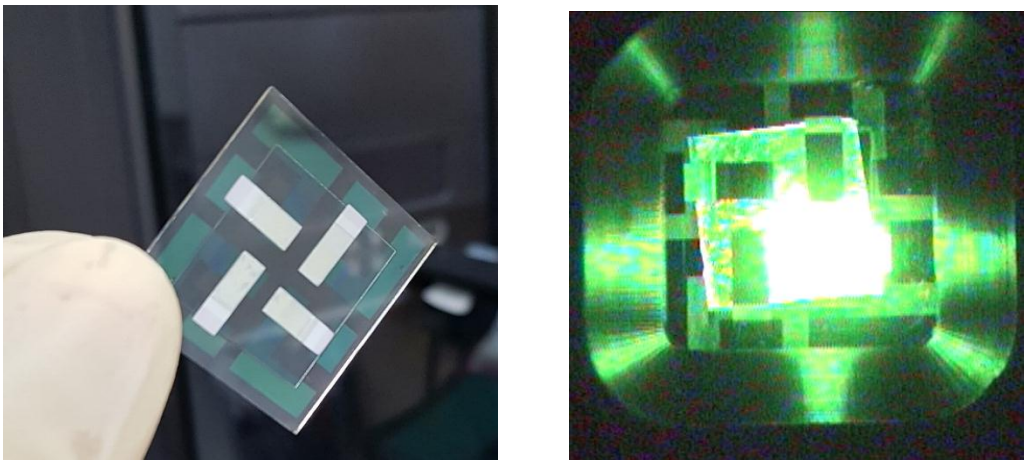


Fig. 3. Luminance of QDLED with various mixed QD-solvents.



(a) *(b)*

Fig. 4. (a) A real QDLED device, (b) A luminescence QDLED device.

Table 1. Summary of the optical and electrical properties of Green-QDLEDs with various solvents for QDs

Solvents	V_{on} (V)	Max. LE (cd/A)	Max. EQE (%)	Max. Luminescence (cd/m^2)
Toluene	8.0	7.31	3.82	3808
Hexane	7.5	8.65	4.01	6448
Octane	8.0	5.12	3.91	5780

3.2. Effect of ZnO nanoparticle Concentrations for device performance

In order to get a balance electron hole to get better emission, the concentration of ZnO nanoparticles to make the ETL layer is also investigated in this work. In a regular QDLED structure, the ZnO thickness also strongly affects the luminescence and efficiency. The spin time was set at 30 s and the thin film was soft baking at 110^{o}C to avoid the damage underneath layer. For the spin rate of the ZnO layer, 2500 rpm was chosen to obtain a thickness of 40 nm, 55 nm, and 62 nm corresponding the concentration of ZnO varied from 20, 30, and 40 mg/ml. The thickness of layers on QDLEDs was observed by Nanoview Systems [10]. Fig. 5 shows the highest maximum luminescence of 9865 cd/m^2, and the driving voltages were around 6.5 to 7.5 V for all concentrations. Improved EQE at 3.68% and luminescence efficiency at 13.84 cd/A were obtained with 30 mg/ml of ZnO, which was the optimized concentration for this device configuration. With this concentration, a 55 nm-thick ZnO thin film creates the optimal conditions for electron transmission through the ETL layer, consequently enhancing the device's performance. Table 2 shows the summary electrical and optical properties of Green-QDLEDs with various ZnO concentrations. The EL peak was 522 nm. The Commission Internationale de l'éclairage (CIE) chromaticity diagram revealed (0.21, 0.75) coordinates with a saturated deep green color (Fig. 6).

Table 2. Sumary of the optical and electrical properties of Green-QDLEDs with various ZnO concentration

ZnO concentration (mg/ml)	V_{on} (V)	Max. LE (cd/A)	Max. EQE (%)	Max. Luminescence (cd/m^2)
20	7.5	10.25	2.69	7021
30	6.0	13.84	3.68	9865
40	7.5	9.78	2.58	5885

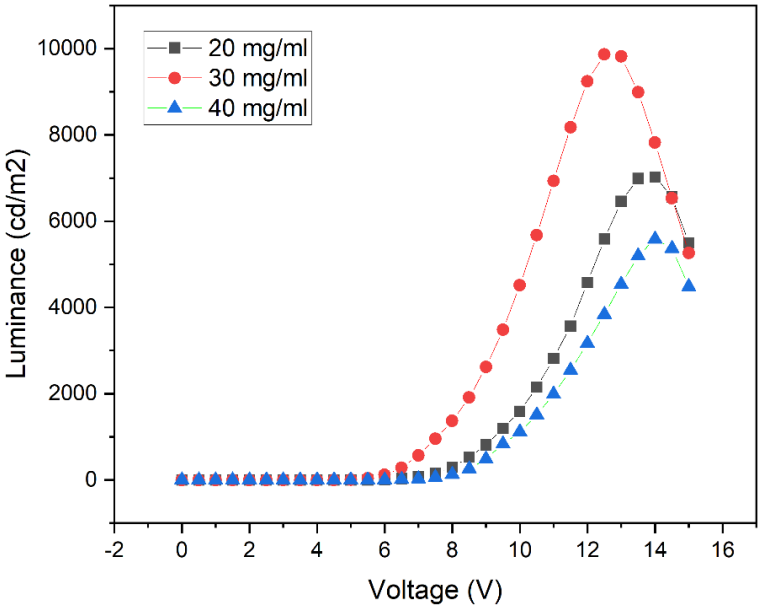


Fig. 5. Luminance of QDLEDs with various ZnO concentration.

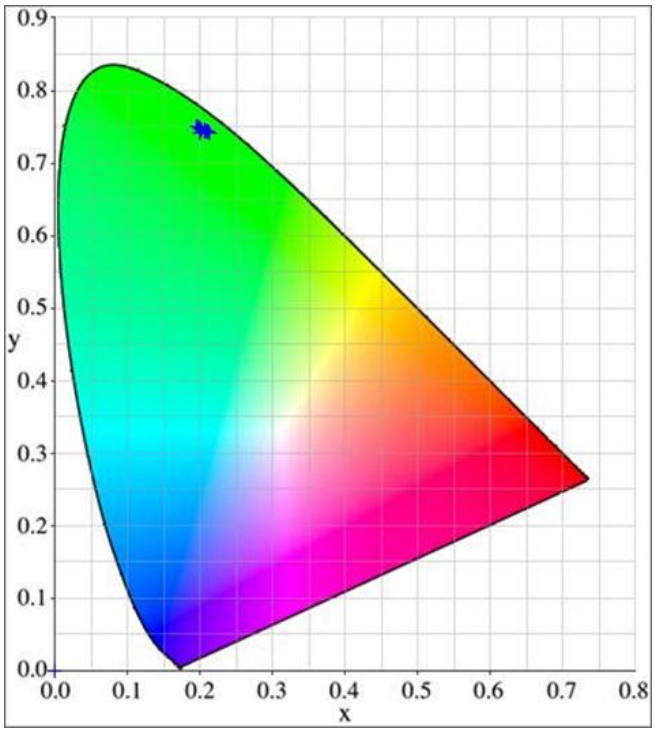


Fig. 6. The CIE color coordinates of the Green-QDLEDs.

4. Conclusion

For all-solution-processed green QDLEDs, the solvent of the emission layer, and the concentration of ZnO nanoparticles were investigated and optimized. The electro-optical properties of hexane-based QDLED are better than those of toluene, octane. When the concentration of ZnO NPs was 30 mg/ml, and the maximum luminescence, the luminance efficiency, the maximum EQE obtained 9865 cd/m^2, 13.84 cd/A, 3.68%, respectively, at a turn-on voltage at 6.0 V. The optimized thickness of 62 nm of ZnO allowed effective electron injection to the EML region and radiative recombination in the Green-QDs with the best electroluminescence properties.

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KHẢO SÁT ẢNH HƯỞNG CỦA CÁC DUNG MÔI VÀ NỒNG ĐỘ ZnO TỚI HIỆU QUẢ PHÁT QUANG CỦA GREEN-QDLEDS ỨNG DỤNG TRONG CÔNG NGHỆ HIỂN THỊ

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Tóm tắt: Điốt phát quang chấm lượng tử (QD-LED) được tập trung nghiên cứu và ứng dụng trong các thiết bị hiển thị thế hệ mới bởi những đặc tính điện và quang vượt trội của vật liệu chấm lượng tử so với những vật liệu truyền thống. Trong nghiên cứu này, vật liệu hạt nano ZnO được tổng hợp và ứng dụng là lớp vận chuyển điện tử trong cấu trúc linh kiện đa lớp. Tiếp đó, điốt QD-LED đa lớp có cấu trúc ITO-Glass/PEDOT:PSS/PVK/Green-QDs/ZnO/Al/Encap được chế tạo bằng các phương pháp quay phủ, bốc bay nhiệt chân không. Ảnh hưởng của các dung môi lên lớp phát xạ cũng như nồng độ dung dịch hạt nano ZnO tới hiệu quả phát xạ của QDLED được nghiên cứu và khảo sát. Với các thông số tối ưu, linh kiện QD-LED đạt cường độ tối đa 9865 cd/m^2, hiệu suất phát sáng là 13,84 cd/A và hiệu suất lượng tử ngoại - EQE là 3,68%, điện áp bắt đầu hoạt động ở 6,0 V.

Từ khoá: *Vật liệu chấm lượng tử; điốt phát quang chấm lượng tử (QD-LEDs); hạt nano ZnO.*

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