Cd-free RGB Electroluminescent Quantum Dot-LEDs Fabricated by Inkjet and Electrohydrodynamic (EHD)-Jet Printing in Ambient Air

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Abstract

Cd-free inverted RGB Quantum Dot (QD)-LEDs were fabricated using air-processed inkjet and electrohydrodynamic (EHD) jet-printing without using a glovebox system, featuring a ZnO nanoparticle ETL and QD/organic nanohybrids, respectively. This approach shows the potential for the utilization of the printing process as a sustainable display fabrication method, reducing the material uses and production costs.

Author Keywords

quantum dots; Cd-free QDs; inkjet; electrohydrodynamic jet printing; EHD-jet; Nanohybrids; QD-LEDs;

1. Introduction

Cd-free quantum dots (QDs) have transformed display technology, offering a high color gamut and cost-effective production [1]. However, the challenge of achieving high-resolution, Cd-free Quantum Dot light-emitting diodes (QD-LEDs) has prompted the exploration of advanced printing fabrication methods. Traditional QD-LED production often requires controlled environments, such as gloveboxes, to prevent air exposure, which can degrade materials [2]. In this study, we explore the potential of combining inkjet-jet and electrohydrodynamic (EHD)-jet printing in ambient air, aiming to simplify the fabrication process and reduce costs for the sustainable display fabrication process. Inkjet printing, a well-established technique for depositing functional layers, was used to pattern the ZnO nanoparticle (NP) electron transport layer (ETL). For higher resolution and finer patterning, EHD jet printing was employed for the emissive layer, using cadmium-free RGB QD/organic nanohybrids. EHD jet printing, capable of producing droplets much smaller than the nozzle diameter (0.001–10 pL), offers precise patterning and supports a wide range of ink viscosities (1–10,000 mPa·s) [3,4]. This study demonstrates the integration of inkjet and EHD-jet printing in ambient air, resulting in printed RGB QD-LEDs with enhanced process efficiency. The use of air-processable materials like ZnO NPs and QD/organic nanohybrids enables the fabrication of complex multilayer structures without the need for controlled environments. Our findings pave the way for more accessible, scalable, cost-effective, and sustainable display fabrication technologies, meeting the demands of next-generation display applications.

2. Experimental

The inverted device design features a transparent ITO cathode, with ZnO NPs (<1 wt% in an alcohol solution) acting as the electron transport layer (ETL, 30 nm). The emission layer (EML) consists of QD/organic nanohybrids (10–30 nm), where InP-based red and green and ZnSe:Te-based blue multi-shell QDs were used. The hole transport layer (HTL) is composed of 4,4',4"-Tris(carbazol-9-yl)triphenylamine (TCTA, 50 nm, Lumtec, LT-E207). Molybdenum oxide (MoO_3, 10 nm, Aldrich, 99.99%) is used as the hole injection layer, and a metallic anode made of Ag (150 nm, Aldrich, 99.99%) completes the structure. The pixel area is defined using hydrophobic pixel-define layers, which are patterned by a lithographic process with a thickness of 0.7 μm on a glass substrate. Each sub-pixel measures 47.5 μm × 95.0 μm with a pixel pitch of 62.5 μm × 110.0 μm.

The ZnO NPs were printed into the pixel-define layer (PDL) on the substrate using an LP50 inkjet system utilizing a KM512 printing head with a 4 pL droplet volume. The QD/organic nanohybrid inks (concentration: 18 mg/mL) with a co-solvent system (QD:n-type:p-type, ratio of 1:1:0.2 by weight) were patterned by in-house developed EHD-jet printing system, followed by drying at 180 °C for 30 minutes in vacuum condition. Both the printing process for ZnO NPs and QD/organic nanohybrids were carried out in ambient air. After the printing process, TCTA and MoO_3/Ag layers were deposited via thermal evaporation in a high-vacuum chamber. Finally, the devices were encapsulated with cover glasses using UV-curable resin for further testing. Electroluminescence (EL) spectra and current density-voltage-luminance (J-V-L) characteristics were measured using a spectroradiometer (Minolta CS-2000) and a source meter (Keithley SMU 236). The EL spectra were measured in a circular area with a diameter of 1 mm.

3. Results and Discussion

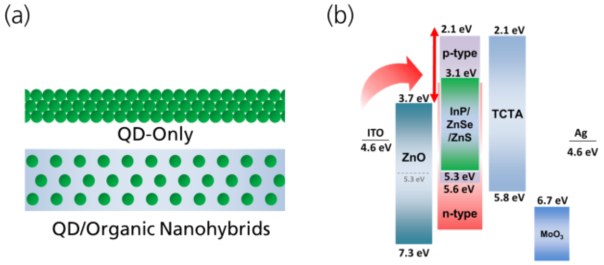

Figure 1. a) A cross-sectional schematic of QD/organic nanohybrids, and (b) an energy band diagram schematic showing their advantages.

The inverted structure (ITO/ZnO/QD-Organic Nanohybrids /TCTA/MoO_3/Ag), shown in Figure 1, was intentionally chosen due to the orthogonal solvent processing capabilities provided by the ZnO NP ETLs. This contrasts with conventional device architectures that use organic HTLs like poly-TPD and PVK. The selection was made to prevent the mixing of organic HTLs and emissive materials (EMLs) during solution-based deposition,

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which often results in reduced device performance [5]. Figure 1b depicts the band diagram of the inverted configuration with the QD/organic monohybrids. For Cd-free inverted QD-LEDs, achieving a proper balance of electron and hole charge carriers is essential for device efficiency and stability [6]. The QD/organic monohybrids, incorporating both n-type and p-type charge transport materials (CTMs), are vital in this regard. By adjusting the ratio and morphology of these materials within the QD/organic nanohybrid layer, the charge balance can be effectively controlled. The p-type material improves hole transport and blocks electron injection into the QDs, while the n-type material complements this function. Furthermore, embedding the QDs within the CTM layer simplifies the process, reduces the number of printing steps, cuts costs, and enhances process stability in air-based environments, as shown in our previous work [7,8]. The composition of the QD/organic nanohybrids system was optimized separately for each color to reduce the parasitic emission from organic materials. To pattern the ZnO layers for the actual inverted QD-LEDs, the ZnO NP inks were printed by inkjet on the structured ITO substrate with a hydrophobic black matrix pixel define layers (PLDs). The selection of the Konica Minolta KM512 printhead is particularly well-suited for the application of inkjet-printed ZnO nanoparticle layers, considering the bank size of 47.5 µm × 95.0 µm and the droplet volume. The KM512 printhead can print droplets as small as 4 pL allowing for precise control over ink deposition, which is crucial for maintaining uniformity and consistency in the printed layers. This fine droplet size ensures that the ink can be deposited within the relatively small space of the bank structure, enabling accurate patterning without excessive spreading or overspill.

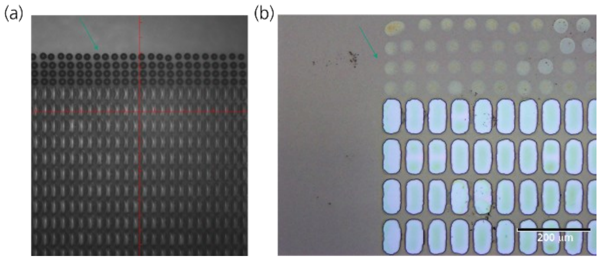

Figure 2. Well-patterned ZnO droplets on the PDLs structure, demonstrating the dewetting behavior of ZnO NP inks: (a) before solvent drying and (b) after solvent drying.

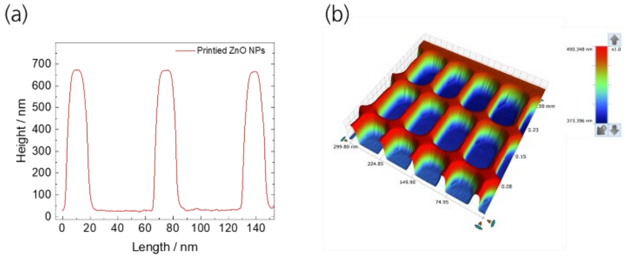

Figure 3. (a) Line profile and (b) 3D profile of a well-filled ZnO NPs (3x2 drops) inside of cavity using Dektak profilometry.

Figure 2 shows well-patterned ZnO NP ink droplets on the PDL structure, illustrating the dewetting behavior of the ZnO NP inks. Due to the hydrophobic nature of the PDL, the droplets initially retract, forming isolated patterns. Interestingly, when two droplets fall on the hydrophobic PDLs, they maintain their separation. However, they can merge to form a single, larger droplet when they are printed inside of bank structure because the bottom ITO has relatively higher surface energy compared to the PDLs. This behavior highlights the interplay between surface tension and the physical constraints of the PDL structure. This merging effect is critical for ensuring a more uniform distribution of the ZnO NP layer, helping to achieve the desired patterning while preventing excessive spreading. The surface profile shown in Figure 3 illustrates the uniformity of the ZnO NP coating, with no visible coffee-ring effects. This indicates a consistent and even deposition process, resulting in a well-distributed ZnO NP layer across the bank structure.

The QD/organic nanohybrid layers were patterned by EHD-jet printing. Figure 4 illustrates the EHD-jet printing principle. A significant voltage is applied between the nozzle and the substrate, creating a Taylor cone at the nozzle tip. This cone formation results from the balance of hydrodynamic force (F_h), capillary force (F_γ), and electrostatic force (F_E) [3]. When the electric field strength exceeds a critical value, a jet emerges from the cone's apex. The jet's properties, such as its size, direction, and pulsation, are influenced by the interplay between the ink and the electric field.

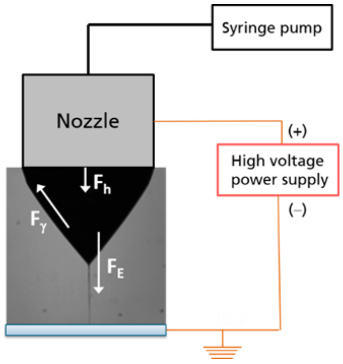

Figure 4. a) Schematic illustration of EHD-jet printing system.

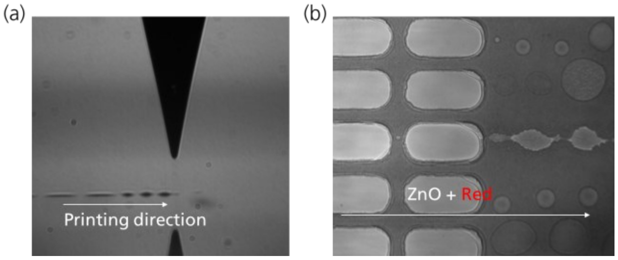

Figure 5. High-resolution patterning process of QD/Organic nanohybrids with EHD-jet printing on a substrate with hydrophobic PDLs.

Figure 5a highlights the capability of EHD-jet printing for QD/organic nanohybrids with continuous mode. As the ink is deposited in lines, the ink becomes separated by hydrophobic PDLs. When the ink is printed onto areas with cavities, droplets form only within the cavities. In contrast, when printed on PDL without cavities, the droplets become smaller and thicker as observed in the dried image shown in Figure 5b. Figure 6 shows the microscopic, PL, and EL images of a fabricated QD-LED device after RGB ink patterning on top of the printed ZnO NPs and the subsequent vacuum deposition of TCTA/MoO_3/Ag to complete the inverted QD-LED structure. Despite the ongoing optimization of the ink printing process, the device demonstrates clean RGB pixel patterning with no visible color contamination, ensuring distinct separation between the color channels. Brightness differences are noted across the pixels, influenced by variations in ink amount and the driving conditions. Nevertheless, this process effectively demonstrates the integration of advanced printing techniques for the efficient patterning of functional layers. The inkjet-printed ZnO NPs and EHD-jet-printed QD/organic nanohybrid inks achieve uniform coverage, contributing to enhanced device performance. Significantly, both printing processes were successfully carried out in ambient air conditions, highlighting the robustness and reliability of the fabrication method.

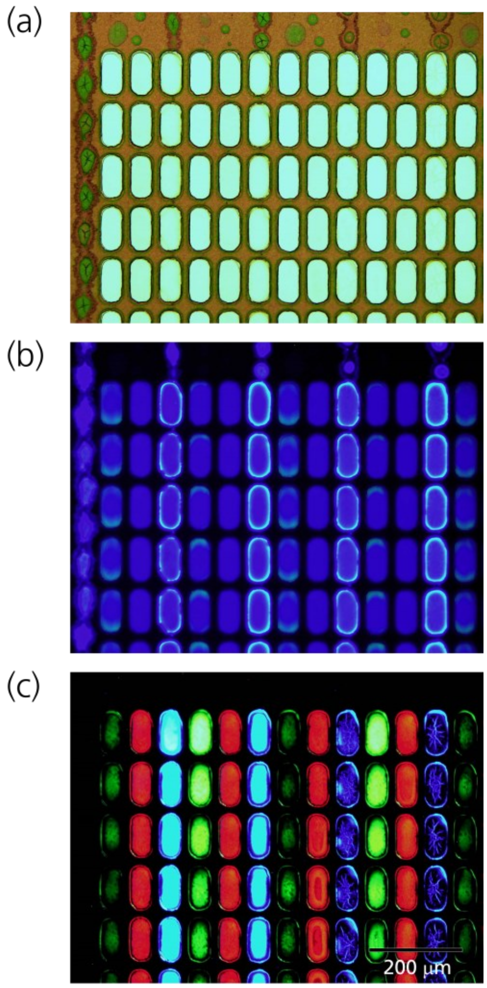

Figure 6. (a) Microscopic, (b) PL, and (c) EL images of printed RGB pixels.

Figure 7 shows EL spectra at various applied voltages, a photo of the working device under a microscope, and a cross-sectional schematic of the developed inverted RGB QD-LED structure. The device with RGB pixel array has a threshold voltage (V_{th}) around 3 V, indicating the efficient charge injection for all red, green, and blue QD/organic nanohybrid devices. The turn-on voltage of the device was around 5 V. The EL spectrum at various voltages shows stronger intensity from the red color, as the RGB pixels are not yet optimized, resulting in stronger emission from the red devices. However, the normalized EL spectrum remains relatively stable across different voltages. The RGB pixels need further optimization of the drying process to achieve uniform layer thickness and improve device performance. Fine-tuning these parameters can lead to the production of high-quality, printed displays.

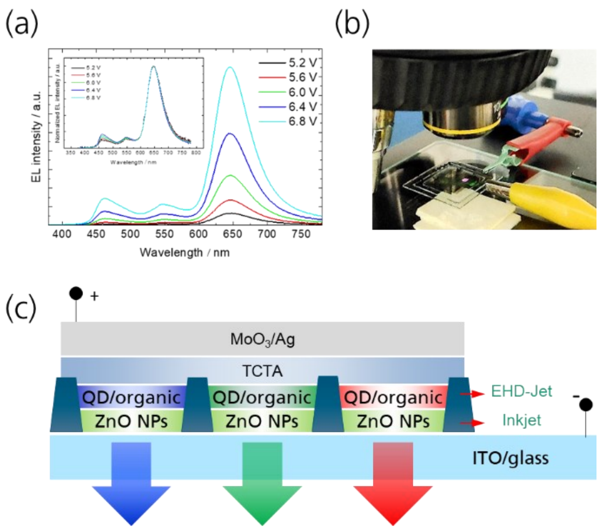

Figure 7. (a) EL spectra at various applied voltages, (b) a photo of the working device under a microscope, and (c) a cross-sectional schematic of the developed inverted RGB QD-LED structure.

4. Conclusion

This study presents the successful fabrication of Cd-free RGB QD-LEDs using inkjet and EHD-jet printing techniques, demonstrating their potential for scalable, cost-effective production of high-resolution devices. By utilizing air-processable materials such as ZnO NPs and QD/organic nanohybrids, we were able to pattern both the electron transport layer and emissive layers, achieving uniform coverage and enhancing device performance. The combination of inkjet-printed ZnO NPs and EHD-jet-printed QD/organic nanohybrids resulted in the pure emission of RGB QD-LEDs with distinct pixel patterns, contributing to improved light emission efficiency. The results also highlight the potential for further optimization, particularly in the drying process and layer thickness uniformity, to maximize the performance of printed QD-LEDs. Notably, both printing processes, carried out in ambient air, underscore the robustness and scalability of the fabrication method, providing a promising pathway for future sustainable fabrication technologies of QD displays.

5. Acknowledgments

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