All Inkjet-printed Cadmium-Free Electroluminescent-Quantum Dot Display at 217 ppi Resolution

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ABSTRACT

We demonstrate the world's first all inkjet-printed Cd-free EL-QD display by successfully overcoming the fabrication- and performance-limiting factors in solution processing. In particular, the intermixing between the stacked layers within the device was eliminated. A study on the critical factors affecting the device performance, including the influence of ETL solvent on quantum dot, is discussed in detail.

1 Introduction

Quantum Dots (QD), due to the unique electro-optical properties arising from quantum confinement within the semiconductor nanoparticles, have attracted much attention from both the industry and academia over the past decade as a candidate for the next-generation display application. [1] With appropriate core-shell structure, they are environmentally stable and free from 'burn-in' effect in extended usage, which the organic-based products in the market undergo. The progress in the synthesis techniques enabled specifically tuned emission spectra and narrow full width half maximum (FWHM) over wide color gamut, which translates into improved contrast ratio, luminance, and resolution of the display panel.

However, much of the advances has been realized through cadmium containing QD, whose toxicity stands as a major obstacle to commercialization. Despite the excellent PLQY (photoluminescence quantum yield) and stability of InP QD on par with cadmium QDs, and multiple reports on improved device efficiency and lifetime with non-toxic QDs, their device characteristics still significantly lag behind cadmium QDs. The difference in performance is usually attributed to the lack of a clear physical understanding of the device operation. While Cd QDs demonstrate similar electron and hole masses, InP QDs show a heavier hole mass. This in turn affects the fermi level adjustment during the device operation with implications for the conduction band maximum and valence band minimum. As a result, electron injection characteristics to QD layer needs further elucidation. [2-5]

Another aspect that requires more discussion is the device architecture of the reported performances. Bottom-emitting structure is the current standard for most reports, where the emission is through the transparent electrode(anode). In order to achieve high aperture ratio for effective commercialization, top-emitting architectures are necessary. They allow a larger emission area unhindered by backplane design, better selection of substrate material, and the exploitation of the micro-cavity effect which enhances the efficiency and color purity. [6–8] Reports on highly efficient top-emitting EL-QD devices have been rare [9–10]. A further implication for Cd-free QDs is that the spectra of these QDs (i.e. InP) are wider than those of Cd-based QDs. Hence the implementation of micro-cavity for Cd-free QDs would be a greater advantage for enhanced color purity in Cd-free-QD-based display.

Over the past decade, much effort has gone into improving device characteristics using a variety of fabrication tools. Most of the reported device performances rely on the traditional spin coating process, which has several shortcomings. It has poor material efficiency, limited manufacturing capacity for large-area, pixelated, and full-color display panels. Among various technologies for large area display, inkjet printing has been regarded as the closest candidate for commercializable fabrication method. Printing in pixel-wise manner would significantly improve material consumption efficiency, and the integration of inkjet process with backplane and module steps is considered relatively simple for the mass production of full-color QD displays.

In this report, we demonstrate for the first time an all inkjet-printed red-green-blue (RGB) Cd-free EL-QD device with top-emission structure [Table 1]. We also address the hurdles needed to be overcomed for successful inkjet printing of QD and electron-transporting layer (ETL) nanoparticles. Systematic studies and optimization of the process parameters and performance of the printing ink were carried out. We identified major degradation factors in device fabrication as the deposition damage (wash-out) and inter-mixing among deposited layers. To utilize the micro-cavity effect for EL devices, we employed a charge transport material which exhibits exceptional thickness control due to its damage-free nature to the underlying layer. Our work opens up a new avenue of approach for EL-QD displays by successfully employing large-area inkjet printing and brings it closer to future commercialization.

Table 1. Summary of inkjet-printed EL-QDs

Color	Cd-free	HIL/HTL	QD	ETL	Reference
R	x	SC	IJP	SC	[11]
R	x	SC	IJP	IJP	[12]

R	x	IJP	IJP	IJP	[13]
R	x	SC/IJP	IJP	SC	[14]
R	o	IJP	IJP	IJP	Our work
G	x	SC	IJP	IJP	[12]
G	x	SC	IJP	EVP	[15]
G	o	IJP	IJP	IJP	Our work
B	x	SC	IJP	IJP	[12]
B	o	IJP	IJP	IJP	Our work

* SC: spin-coating, IJP: Inkjet printing, EVP: Evaporation

2 Current Status of EL-QD Display Technology

Figure 1 describes some of the recent progress in Cd-free EL-QD device performances. [16] It is clearly shown that Cd-free EL-QD device performances have rapidly evolved over the past decade. In particular, red EL-QD devices reached EQE of over 20% and T_{50} lifetime of over 1 million hours at 100nit. [17–18] Blue EL-QD also achieved EQE of over 20% and T_{50} lifetime of over 15,000 hours at 100nit. [19] With the current pace of intense research, it is expected that RGB EL-QDs will reach EQE of over 20% and T_{50} lifetime of 1 million hours at 100nit in a few years.

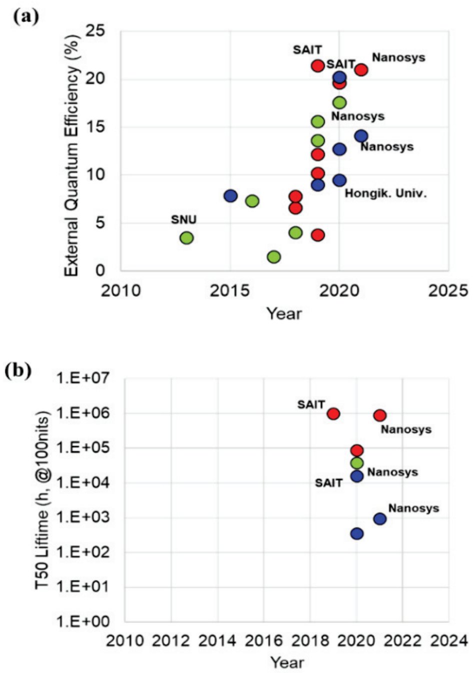


Figure. 1 (a) Progress of Cd-free EL-QD efficiency, (b) Progress of Cd-free EL-QD lifetime

For mass production of EL-QD display, inkjet printing is believed to be the most feasible tool capable of full-color pixel-wise patterning. Quantum dots are susceptible to degradation by heat, which is one of the most common side-product of other industrial processes such as vacuum evaporation that is used in commercial OLED panel production. Further, QDs are usually synthesized and stored in the solution form, and therefore its implementation in inkjet printing can be easily modulated by adequate ink formulation strategy. Also, the level of maturity of inkjet printing technology, including inkjet printers and ink materials, has increased significantly over the past years. [20]

Figure 2 compares EL-QD panel prototypes for demonstration from a number of panel makers with currently commercialized display applications in terms of panel size and pixel resolution. It shows a trend that the panel makers aim to develop the EL-QD display for large-sized applications like TV and monitor. Due to the resolution limit of inkjet printing, the EL-QD is currently considered infeasible for mobile applications.

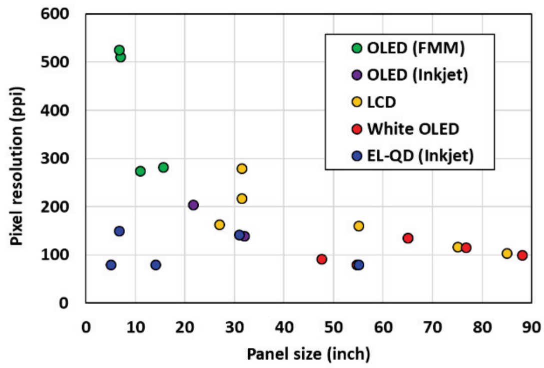


Figure. 2 Panel size vs. pixel resolution according to display technology. EL-QD demo panels are publicly announced in conferences [21, 22,23]

3 Results and Discussion

3.1 Optimization of QD ink formulation

An adequate QD ink formulation design is necessary for stable jetting and drying during the inkjet process. The ink, composed of the solute and solvents, is rigorously formulated in such a way that the physical properties that govern important process parameters for inkjet printing, namely boiling point, surface tension, and viscosity, fall within a favorable range. The combination of these properties determines the jettability of the ink and uniformity of the deposited thin film. The rheology should be adjusted for a spectrum of resolution targets as the droplet size, which ranges in pico-liters depending on the application, dictates the process control. The long-term stability of the ink itself must be examined as adverse phenomena such as phase separation, aggregation and sedimentation can occur if the formulation is poorly executed. Reynolds number (N_{Re}), Weber number (N_{We}) and the inverse of Ohnesorge number (Z), all of which are related to the viscosity, surface tension and density as shown in the following equations, help to characterize an ink droplet [24].

$$N_{Re} = \frac{v\rho a}{\eta}$$

$$N_{We} = \frac{v^2 \rho a}{\gamma}$$

$$\mathrm{Oh} = \frac{\sqrt{N_{We}}}{N_{Re}} = \frac{\eta}{\sqrt{\gamma\rho a}}, \quad \frac{1}{\mathrm{Oh}} = Z$$

where ρ, η and γ are the density, dynamic viscosity and surface tension respectively. The velocity of the fluid is represented as v and α is in the dimension of length.

The printability range of Z is within the limit $4 \le Z \le 14$. In case of $Z < 4$, the droplet filament is elongated and the time for droplet generation is extended. Droplet formation is inhibited when $Z > 14$. The vapor pressure of the QD solution plays an important role in the drying phase because premature drying results in an unwanted stain on the panel [25]. The solvent with inadequately low boiling point can easily dry on the surface of the inkjet head nozzle and the aggregated material eventually blocks the nozzle. Conversely, if the boiling point is too high, it becomes very difficult to remove the residual solvent on the dried film. To find the 'right spot', we introduced a mixed solvent system for inkjet-printing. Z of the proposed system is around 8.5, which is within the printability range.

For the fabrication of EL-QD devices by inkjet printing, the precision of ink placement on the surface is important. Drop placement accuracy (DPA) is a method to check ink printing accuracy by recording the position of the printed drop on the substrate. Fig. 2 shows a more precise placement for QD ink B compared to QD ink A. QD ink A is pristine QD that is unmodified after the synthesis, and therefore contains native ligands such as oleic acid (OA). We performed a ligand exchange reaction from carboxylic acid anchor ligand to various thiol anchor materials for QD ink B. The shorter-chained thiol-based ligands improves the electron transporting characteristics due to the shorter distance between the QDs compared with oleic acid (OA). Given that the two inks differ only in the organic material content, TGA analysis was performed. TGA analysis in Figure 3 shows that QD ink B, which has higher organic material ratio (14.2%), is more stable than QD ink A (11.2%) for inkjet printing.

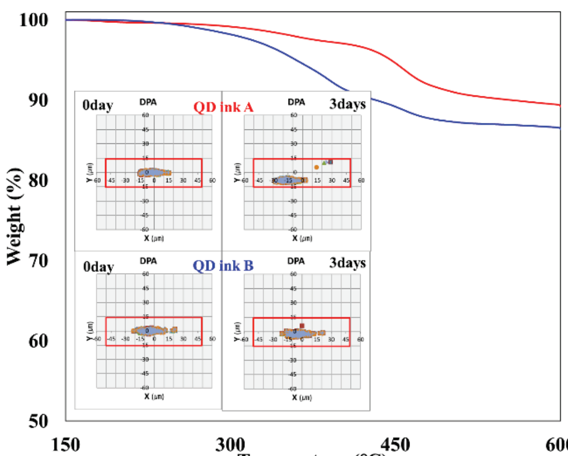
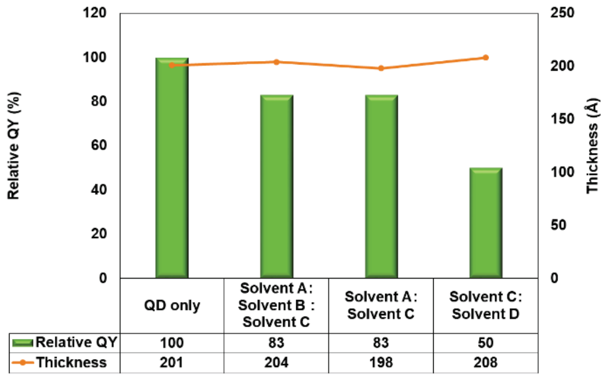


Figure. 3 Thermogravimetric analysis (TGA) and drop placement accuracy (DPA) of two types QD inks

3.2 Optimization of ETL ink formulation

In order to achieve better efficiency and lifetime of EL-QD devices, the development of appropriate ETL is critical. ZnMgO is a suitable ETL for EL-QD device due to their optoelectric properties. To make ZnMgO inkjet-capable, equally suitable ink formulation is needed. When the ink is dropped on the surface of a thin film, dissolution of the underlying layer can occur, and re-formation of the layers results in intermixing. EML and ETL intermixing especially detrimental to device performance. The resistance of QD films to the ETL solvents was pre-screened by PL intensity and ellipsometry measurements. Changes in quantum yield(QY) can be observed before and after rinsing of the ETL solvent in Figure 4. Since the thickness of the QD film is unchanged, it implies that the QD film is not physically removed, but the solvent damages the surface of the QD. Previous studies have shown that the decrease in PL-QY of QDs occurs when exposed to alcohol-based protic solvents or during purification [26]. Since some hydroxyl groups are present in the solvent system, damage will occur if the surface passivation of the QD is incomplete. Also, the relatively high boiling point of the ink increases the exposure window of the solvent to QD. In addition, high-polarity solvent D enhances the damaging effect on the QD surface.



	QD only	Solvent A : Solvent B : Solvent C	Solvent A : Solvent C	Solvent C : Solvent D
Relative QY	100	83	83	50
Thickness	201	204	198	208

Figure. 4 QY and thickness of QD film after rinsing with ETL solvents

3.3 All inkjet-printed EL-QD

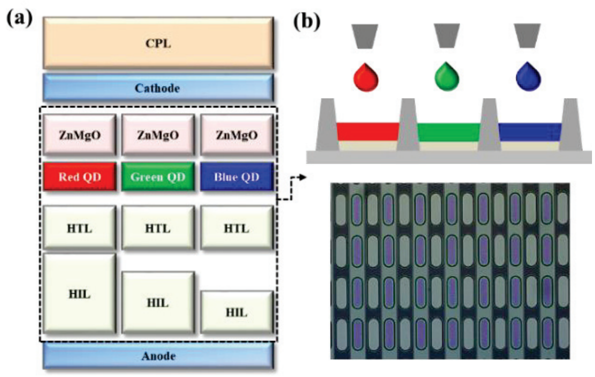


Figure. 5 (a) Schematic of the all inkjet-printed EL-QD devices. (b) Concept diagram of inkjet printing and architecture of substrate

Figure. 6 6.95” 217 ppi inkjet-printed Cd-free EL-QD

For top-emission structure, hole injection layer (HIL) and HTL were deposited on the ITO/Ag/ITO substrate with a repellent pixel-defining-layer bank. All inkjet-printed layers were deposited in ozone-free environment where ozone level was maintained to be less than 1 ppb. Baking process after each deposition was conducted in nitrogen-filled chambers. After RGB QDs and ZnMgO were deposited on the HTL, cathode and CPL were thermally evaporated. We successfully fabricated 6.95” 217 ppi Cd-free EL-QD top-emission display panel (Figure 6).

4 Conclusion

In conclusion, we successfully developed the world’s first all-inkjet-printed Cd-free EL-QD display based on the optimized ink formulation. In order to proceed to mass production, it is necessary to close the performance gap with OLED, which requires further improvement in the QD material and fine-tuning the device fabrication process. We have studied QD and ETL ink formulations to improve the performance of inkjet printing based device. Especially, the selection of QD and ETL solvents was identified as one of the key factors in improving the inkjet-printed device performance, which also influence the efficiency of QD and stability of inkjet printing. We believe that our work contributes toward the realization of commercial EL-QD display through in-depth analysis of the QD and ETL ink formulation.

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