Siloxane-encapsulated Quantum Dot Film and Inkjet-printed Pattern Formation for QD-OLED Devices

Byung Doo Chin[1], Yoon-Jeong Choi[1], Jeong-Yeol Yoo[1]
Chil Won Lee[2], Jang Sub Kim[1]

bdchin@dankook.ac.kr
[1]Dept. of Polymer Science and Engineering, Dankook University, Yongin-si, Gyeonggi-do, 16890, Korea
[2]Dept. of Chemistry, Dankook University, Dongnam-gu, Cheonan-si, Chungcheongnam-do, 31116, Korea
Keywords: Quantum Dot, Encapsulation, Color Conversion, Inkjet Printing

ABSTRACT

We have fabricated color patterning pixels of quantum dot (QD) based on the efficient blue OLEDs and inkjet-printed red/green QD color conversion layers. Synthesized QDs were encapsulated with siloxane using a ligand substitution and reverse micro-emulsion. Uniformity of QD pattern, photoluminescent quantum yield, stability, and QD-OLED conversion performance was investigated.

1 Introduction

Colloidal quantum dots have garnered significant attention because of their size-tunability color-tunability, high color purity, high quantum efficiency, and photoluminescence quantum yield (PLQY). Although red and green emitting QDs with almost perfect efficiency have been reported [1], their LED devices generally suffer from less-stable device operation (lifetime) compared with organic light emitting diodes (OLEDs). Therefore, application of red/green QD color conversion layer (CCL) combined with an efficient blue OLED is feasible approach for more distinguished large area display. In order to pattern QD-CCLs, photolithography and inkjet printing method are widely studied [2,3]. The photo-lithography is useful for large scale fabrication processing of color filters, but if the QD is not stable for light exposure, only a limited process (positive resist/lift-off) can be applied, and the chemicals used in the resist stripping steps might attack the emitters. Inkjet printing is simpler, and material-efficient method compared to photo-lithography, since it only prints within the desired area using the infinitesimal amount of ink (in case of drop-on-demand process).

In this study, to achieve the stable QD-patterned pixels or printed films toward an efficient color conversion device, a mixture of siloxane-encapsulated QDs and light diffuser nanoparticle is formulated for a pattern-printing by inkjet process. Fabrication of an efficient blue OLED (here, we have employed boron-based blue thermally activated delayed fluorescence materials) with evaporated stacks was also an important step for QD-CCL full color QD-OLED device. To improve a stability of the red and green QD-CCLs, siloxane coating process for QDs was optimized using ligand modification reaction and reverse micro-emulsion method. Followed by the mixture formulation of surface engineered QDs and light diffusers, parameters for ink such as surface tension, viscosity, and vapor pressure were tuned for the uniform pixel printing.

2 Experiment

CdSe/ZnS red (RQD) and green (GQD) (10 wt% in toluene) were purchased from HYESUNG Co. Ltd. (Korea). Efficient and stable siloxane-encapsulated QDs were obtained by ligand substitution and reverse micro-emulsion method. First, ligand substitution reaction was performed by adding 0.7 mL of (3-mercaptopropyl) methyldimethoxysilane (MPMDMS) in 10 mg/mL toluene QD solution and stirring for 24 h in the dark room. Then, excess of ethanol was added to precipitate MPMDMS-capped QD (MQD) and re-dispersed in hexane for 3 times. The mixture was centrifuged at 3,600 rpm for 15 min, and the resulting MQDs were re-dispersed in cyclohexane for further siloxane encapsulation reaction. The siloxane encapsulated QDs were prepared using reverse micro-emulsion process. First, 2.5 mL of IGEPAL CO-520 (Mn 441, Sigma), 0.3 mL of distilled water, and cyclohexane (8 mL) mixture were stirred vigorously for 30 min. Next, 2 mL of MQD solution in cyclohexane and 0.3 mL of 3-mercaptopropionic acid (MPA) was introduced in the solution and stirred for 1 h to make additional ligand substitution with MPA. In this step, additional ligand exchange reaction was performed with MPA ligands having a hydrophilic property for better introduction of QDs into reverse micro-emulsion. Then, 6 mL of NH_4OH and 0.2 mL of tetraethyl orthosilicate as silane precursors were added in the above solution at 15 min intervals and stirred for 24 h. The ethanol was employed to break the above micro-emulsion solution, and then, the resulting products were washed two times with ethanol and hexane by centrifugation and ultrasonication. The methods of siloxane-encapsulation for commercial CdS/ZnS QD core/shell were also modified for custom-synthesized InP/ZnSeS/ZnS QDs,

such as 2,2'-bipyridyl or other-type ligand exchange and reverse micro-emulsion. Prepared QDs were formulated with various solvent mixtures for further optimizing test for inkjet printing. Dispersion of TiO_2 and other nanoparticles for optical diffusing effect with various size distribution was prepared and then blended with QD inks.

The materials used for the blue OLED device were as follows ; 1,4,5,8,9,11-Hexaazatriphenylene-hexacarbo nitrile (HAT-CN), 4,4'-Cyclohexyldienebis[N,N-bis(4-methylphenyl) benzene amine] (TAPC) 1,3-bis(N-carbazolyl)benzene (mCP), 3,3"-di(9H-carbazol-9-yl)-1,1':2,1"-terphenyl (DCz-oTP), N7,N7,N13,N13,5,9,11,15-octaphenyl-5,9,11,15-tetrahydro-5,9,11,15-tetraaza-19b, 20b-diboradinaphtho [3,2,1-de:1',2',3'-jk]pentacene-7,13-diamine(v-DABNA), Diphenyl-4-triphenylsilylphenyl-phospine oxide (TSPO1), 1,3,5-Tri[(3-pyridyl)-phen-3-yl]]benzene (TmPyPb), Inkjet printing properties were evaluated using a commercial inkjet printer, Omnijet 300 (Unijet, Korea) equipped with Fujifilm sapphire nozzle (QS-256/10AAA).

3 Results and Discussion

Fig 1(a)(b) shows the electroluminescence spectrum of blue v-DABNA as a hyperfluorescent material in blue OLED, with an emission peak of 474.8 nm, and a narrow full width at half maximum (FWHM) of 28 nm. The multiple resonance effect of the boron and nitrogen atoms makes the localization of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) on each atom. The resulting non-binding molecular orbitals reduced the vibronic coupling and vibrational relaxation in the material, realizing of blue emitters with sharp FWHM [4].

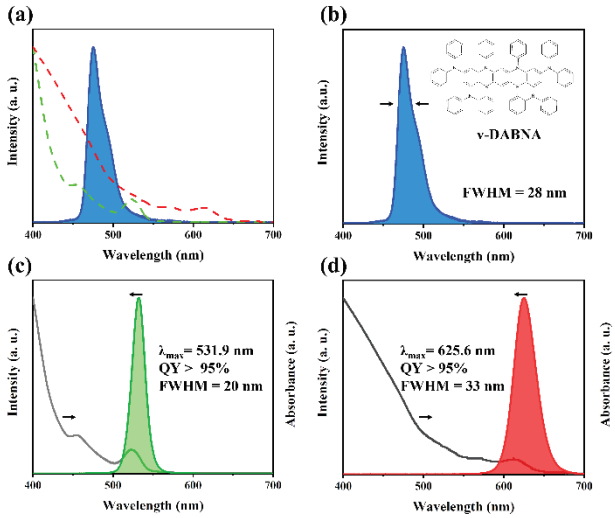

Fig.1 (a)(b) Comparison of EL spectrum of v-DABNA as a hyperfluorescent material in blue OLED and absorbance spectra of GQD (green dash line) and RQD (red dash line), (c)(d) absorbance and photoluminescence spectra of GQD and RQD.

As manifested in Fig 1(c) and (d), GQD and RQD exhibit peak emissions at 531.9 and 625.6 nm with FWHM of 20 and 33 nm, respectively. Both red and green QDs strongly exhibit absorption in blue light region with short wavelength in the absorbance spectra, and have high PLQY of 95% or more, showing that they are suitable for utilization as emitters of the CCLs.

Fig 2. shows the PL intensity and PLQY changes of RQD and siloxane-encapsulated RQD under harsh conditions such as thermal annealing [Fig 2(a)-(c)], and exposing under UV-irradiation [Fig 2(d)-(f)]. The PL intensity of the un-encapsulated, pristine RQDs dropped extremely, and the PLQY was measured to be 23% compared with initial PLQY of 95%. This represents a huge drop of 72% decrease in the PLQY after 7 days under thermal annealing. Siloxane-encapsulated RQD maintained 89% of the initial intensity at the same thermal annealing condition, showing a value of 79% PLQY after 7 days of annealing (85% initial PLQY).

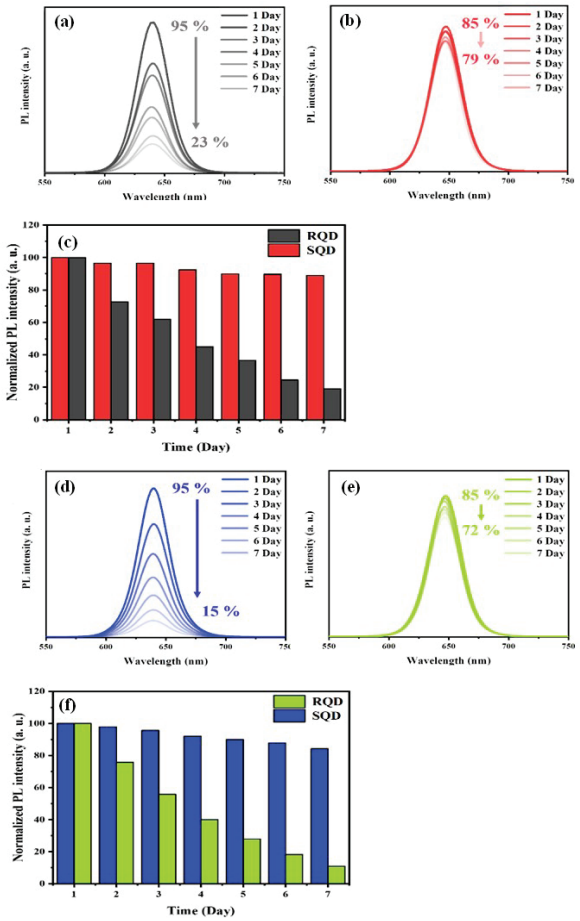

Fig. 2 Comparison of PL intensity; initial and final PLQY of the (a)(d) (un-encapsulated) RQDs, (b)(e) siloxane-encapsulate RQD. Histograms - changes in relative PL intensity of each QDs (c)(f). Data (a-c) for thermal annealing at 120°C, and UV-irradiation (d-f)

Similarly, at a photostability test, the PLQY of pristine RQDs showed huge drop of 80% decrease under 7 days UV-irradiation. Conversely, siloxane encapsulated QD showed a PLQY as high as 72% after 7 days of test, retaining 84% of the initial intensity of RQD. Both for thermal annealing and UV-irradiation evaluation, it was confirmed that siloxane-encapsulated QDs showed significant improvement of stability compared with the untreated QD.

Fig.3 (a) illustrates the schematics of blue hyperfluorescent OLED-QD CCL pixels. Sample image of QD ink dispersions were shown in Fig. 3 (b). The initial results of inkjet-printed patterns of GQD/RQD emitters are shown in Fig 3(c) and (d), where the former illustrates the jetting flight images at the optimized voltage-pulse signal of piezoelectric nozzle. Printed QD patterns, as seen in Fig 3(d) without TiO_2 scatters, forms significantly thin layer (3D microscopic image revealed that only 23 to 57nm-thick-scale GQD patterns). However, thicker and parabolic pattern profile was obtained in a case of GQD/TiO_2/acrylic resin ink prepared as CCL layer [Fig 3(e)]. Such a viscous ink with high solid loading generally required higher bias voltage signal and sufficient duration (dwell) time for jetting condition. It is important to design an appropriate thickness and coverage of QD-CCL pixelated area for green/red emitting region, since the color-conversion might result in an incomplete state at the insufficient thickness of CCL, as seen in Fig 3(f). This affects also the FWHM of converted light to be broad (especially for green QD-CCL). We have further optimized the solid contents and ratio of QD / light diffuser (nanoparticle) mixture toward an enhanced compatibility of the encapsulated QD materials. Based on the quantitative analysis of the peak area of conversion (with quantum yield at integrating sphere), degree of blue leakage at green and red-conversion depending on the composition of printed and pixelated QD-CCLs will be characterized. Blue OLED light (476nm EL peak, EQE 6.2 @1000nit, maximum 17%, CIE 1931 0.14, 0.18) in comparison with a commercial blue LED source spectra will be evaluated for better understanding of OLED to QD conversion behavior.

4 Conclusions

We have demonstrated red/green QD-patterned pixels with an efficient blue hyperfluorescence OLED light source. To obtain QD-CCLs that can be solution-processed in the ambient condition, the red and green QDs were encapsulated with siloxane, showing only 6-13% of reduction after 7 days thermal annealing and UV-irradiation test. We have formulated stabilized QD-CCLs, where more appropriate control of thickness and compatibility between QD-light diffuser, such as ratio of compositions/size distribution, will be further studied in detail. Our research can possibly contribute to achieve the higher efficiency and lower fabrication cost of QD CCL/blue OLED device for full color display applications.

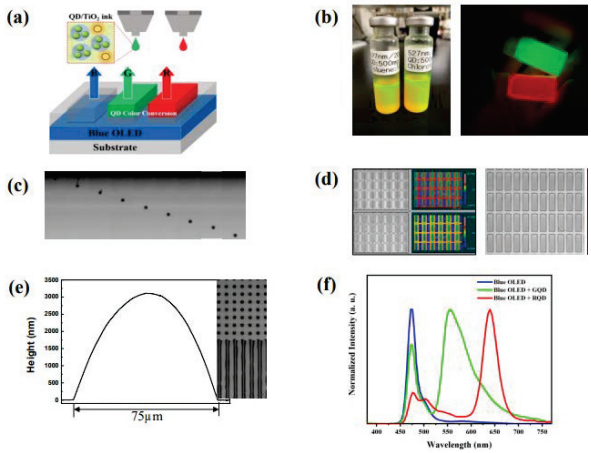

Fig. 3 (a) Schematic illustration of QD CCL/blue OLED (b) photographs of QD solutions (c) Flight of ink droplet of RQD in a jetting cycle (d) Inkjet-printed pixels of GQD/RQD in the pixel-defining insulated layer (e) Printed pattern; RQD/TiO_2/acrylic resin with > 3um thickness dot/line pattern (f) Color conversion spectrum of GQD/RQD with blue OLED (0.14, 0.18) light source.

Acknowledgment

This research was supported by the industrial strategic technology development program (20011059, Development of inks for emitting layers with high performance and long lifetime for printing process, funded by MOTIE, Korea)

References

[1] Y.-H. Won, O. Cho, T. Kim, D.-Y. Chung, T. Kim, H. Chung, H. Jang, J. Lee, D. Kim, E. Jang, "Highly efficient and stable InP/ZnSe/ZnS quantum dot light-emitting diodes" Nature Vol 575, pp 634-638 (2019)

[2] Y. Wang, I. Fedin, H. Zhang, D.V. Talapin, "Direct optical lithography of functional inorganic nanomaterials", Science, Vol 357, pp 385-388 (2017)

[3] Z. Hu, Y. Yin, M.U. Ali, W. Peng, S. Zhang, D. Li, T. Zou, Y. Li, S. Jiao, S. Chen, C.-Y. Lee, H. Meng, H. Zhou, "Inkjet printed uniform quantum dots as color conversion layers for full-color OLED displays" Nanoscale, Vol 12, pp 2103-2110 (2020)

[4] Y. Kondo, K. Yoshiura, S. Kitera, H. Nishi, S. Oda, H. Gotoh, Y. Sasada, M. Yanai, T. Hatakeyama, Nat. Photonics, Vol 13, pp 678-682 (2019)