Wide Color Gamut White Light-Emitting Diode using Quantum Dot/Siloxane Hybrid Encapsulation Material with Excellent Environmental Stability

Junho Jang[1], Da-Eun Yoon[2], Seung-Mo Kang[1], Ilsong Lee[2], Doh C. Lee[2], and Byeong-Soo Bae[1]

[1]Wearable Platform Materials Technology Center (WMC), Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea

[2]Department of Chemical and Biomolecular Engineering, KAIST, Daejeon 34141, Republic of Korea

Keywords: Quantum dot, Siloxane hybrid, Stability, Encapsulation, White light-emitting diode.

ABSTRACT

We report a luminescent light-emitting diode (LED) encapsulation material using quantum dot (QD)/siloxane hybrid (TSE-QD). The TSE-QD shows exceptional stability under high temperature (120 ℃ in ambient) and various chemicals. TSE-QD based white LED also exhibits superior reliability under high temperature/high humidity and wide color gamut (116 % of NTSC).

1 INTRODUCTION

The development of white light-emitting diodes (LEDs) is important for full color display and lighting. Commonly, white LEDs have been obtained by combining a blue LED chip with yellow luminescent converters in which $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) and Sr_2SiO_2:Eu are used as color converters to achieve white lighting for backlighting and general illumination. Although the white LEDs that use phosphors have high color rendering index (CRI) values (> 80), they are not suitable for high-resolution display applications due to their broad emission band and low color purity (i.e., poor color gamut). This make them unable to express the natural color of objects [1].

Quantum dots (QDs) are promising color converting materials for next-generation display application due to their unique optical properties such as size-dependent color tunability, high color purity, wide color gamut and high photoluminescence (PL) quantum yield (QY). However, the vulnerability of QDs to oxygen and moisture is a huge obstacle to practical application because they can be significantly damaged during device fabrication and long-term operation. The commercialized QD for display has been a form of color converting QD films in liquid crystal display (LCD) backlight unit (BLU) using blue LED (i.e., On-Surface type), where QDs were physically blended in polymeric matrices sandwiched between two barrier layers that protect from oxygen and moisture. [2] It is more desirable for LCD BLU using white LEDs encapsulated the QDs directly into the packaging (i.e. On-Chip type) in terms of performance and cost. Nevertheless, LEDs with encapsulated QDs have not been used in display applications due to their fatal instability. Although dispersion of QDs in conventional optical resin has been attempted via additional processes, several problems, for example, uniform dispersion of QDs and instability of white LEDs under high temperature and humidity, still remain as obstacles to commercialization. Therefore, reliable LED encapsulating materials that contain uniformly dispersed QDs in thermally stable optical resin should be developed without the need for additional protecting layers. [2]

Previously, we reported a UV-Curable QD/Siloxane composite (PSE-QD) film based on sol-gel derived methacrylate functionalized siloxane hybrid with high thermal stability for On-Surface type application. [2, 3] However, the PSE-QD film has several limitations for On-Chip type application such as (i) difficulty for complete curing due to UV absorption of the QDs, (ii) low temperature deterioration of methacrylate groups, and (iii) the necessity of using thermal curing for LED encapsulation. Therefore, thermally curable QD-dispersed LED encapsulating materials with high stability in extreme thermal and humid conditions should be developed.

In this study, we report a thermally curable QD/siloxane hybrid (TSE-QD) fabricated using CdSe/CdZnS core/shell QDs encapsulated in a thermally resistant siloxane matrix with high refractive index (> 1.57). [4] The TSE-QD was fabricated via thermal-induced polymerization (i.e., hydrosilylation reaction) of linear-structured oligosiloxane resin in which the QDs were dispersed (QD/Siloxane resin). [5, 6] The QDs were uniformly dispersed in a linear-structured siloxane matrix and retained their initial optical properties during the high temperature fabrication process. Notably, we achieved dramatically enhanced thermal and chemical stability. Finally, we demonstrated a white LED using a blue LED chip directly encapsulated by yellow emitting TSE-QD, where red and green QDs were mixed in a ratio appropriate to obtain the natural white.

2 EXPERIMENT

The entire fabrication process of TSE-QD is depicted

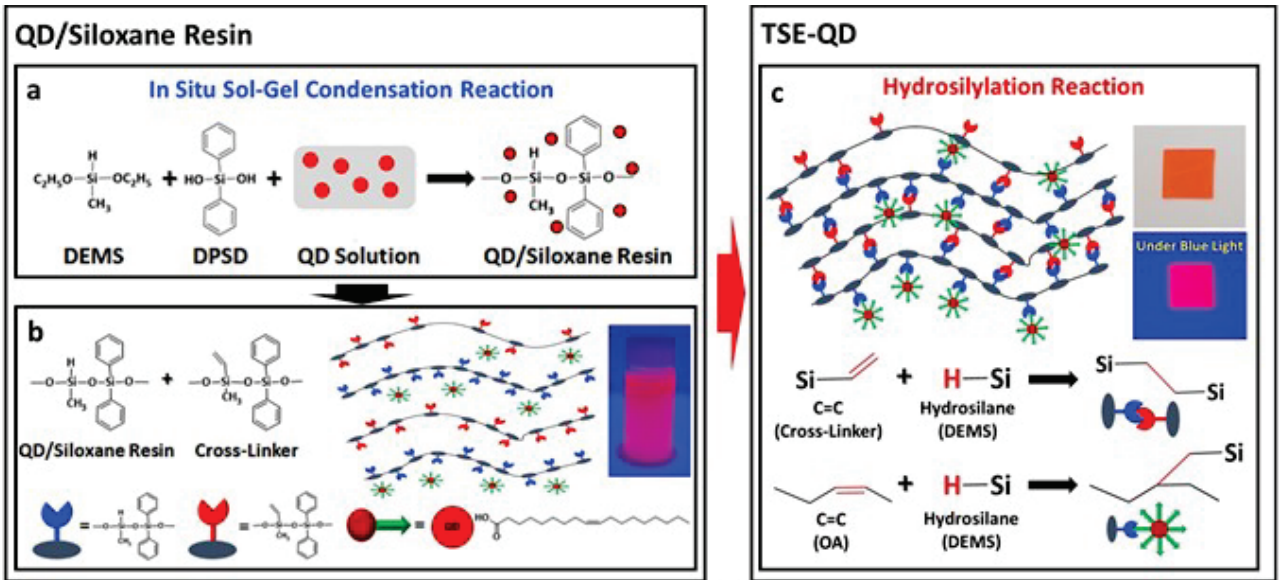

Fig. 1. Entire fabrication process of TSE-QD film

(a) In situ sol-gel reaction between ethoxy groups (DEMS) and hydroxyl group (DPSD) in the presence of QDs. (b) Mixing the QD/Siloxane resin with cross-linker (vinyl-based siloxane resin). (c) Thermal-induced hydrosilylation reaction between hydrosilane group of DEMS and C=C bonds of cross-linker and oleic acid. [8]

in Fig. 1a-c. [7] First, QD/Siloxane resin was synthesized via an in situ sol-gel condensation reaction between the ethoxy groups of DEMS and hydroxyl groups of DPSD in the presence of CdSe/CdZnS QDs passivated by OA (Fig. 1a). In this step, the hydrophobic interaction between organic functional groups (hydrogen and phenyl groups) and surface ligands (OA) induces homogeneous distribution and encapsulation of QDs during the sol-gel reaction.[22] Second, the as-synthesized QD/Siloxane resin was mixed with cross-linker for the thermal-curing process (i.e., hydrosilylation reaction) (Fig. 1b). The cross-linker was also used as sol-gel derived vinyl-based siloxane resin. The resulting viscous QD dispersed siloxane resin showed no aggregation of QDs in the matrix, and retained PLQY during synthesis processes (see the inset photograph in Figure 1b). Last, TSE-QD was fabricated via a thermal-induced hydrosilylation reaction, which causes cross-linking of vinyl (C=C) groups and hydrosilane (Si-H) groups (inset image of Fig. 1c). As shown in Fig. 1c, the carbon single bonds can be formed through two cross-linking pathway during the hydrosilylation process: (i) the reaction between vinyl groups of the siloxane cross-linker and hydrosilane groups of the QD/Siloxane resin, and (ii) the reaction between vinyl groups of the QD surface ligands (i.e., OA) and hydrosilane groups of the QD/Siloxane resin. [7] Two cross-linking pathways provide dense encapsulation of QDs by the siloxane matrix.

3 Results and Discussion

We investigated the stability of TSE-QD under high temperature aging conditions. For comparison, previously fabricated PSE-QD, which has branched siloxane networks, and the commercial acrylate polymer mixed with QDs (QD/Acrylate), which is composed of a diacrylate functionalized hydrocarbon backbone without siloxane bonds, were also tested. The QD/Acrylate was prepared by simple mixing of a QD solution with acrylate resin solidified by UV-curing. Fig. 2 displays the change of PLQY of TSE-QD, PSE-QD, and QD/Acrylate monitored for 30 days at 120 ℃ and 5 % relative humidity (RH) condition. The TSE-QD film showed much less degradation (about 20 % decrease) compared to the previous PSE-QD (about 80 % decrease) and QD/Acrylate (diminished optical property) after aging for 30 days.

To provide a practical application, we demonstrated a

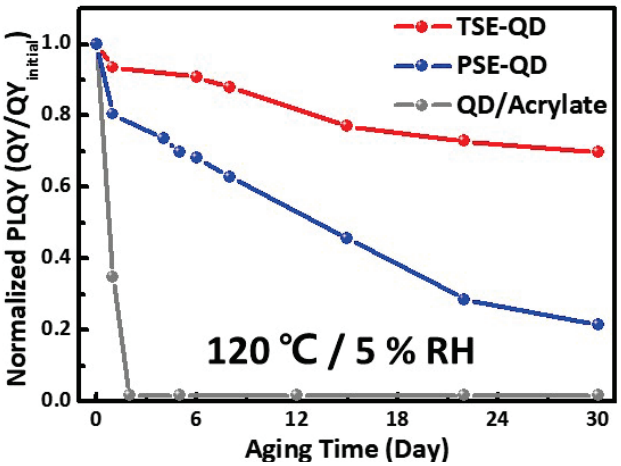

Fig. 2. Result of thermal stability test

(a) Changes of PLQY of TSE-QD (red), PSE-QD (blue), and QD/Acrylate film (black) aged at 120 ℃ / 5 % RH for 30 days. [8]

white LED that uses a yellow emitting TSE-QD (yellow TSE-QD) and blue LED chip. To achieve the yellow emitting QD/Siloxane composite, we additionally fabricated a green emitting TSE-QD (green TSE-QD) via the in situ sol-gel reaction and thermal curing process (Fig. 3a). By optimizing the ratio of red QDs and green QDs in TSE-QD (the weight ratio of green QD to red QD was 4 to 1), yellow emitting QD/Siloxane resin and TSE-QD (yellow TSE-QD) were obtained as shown in Fig. 3b

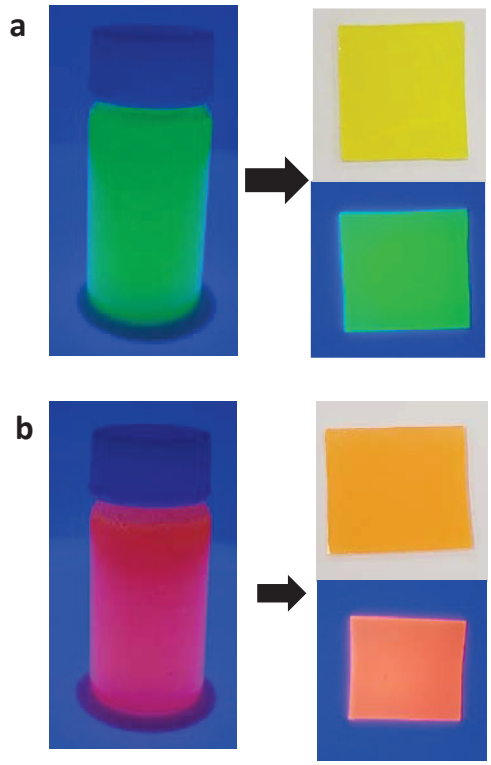

Fig. 4. Photographs of QD/Siloxane resin & TSE-QD
(**a**) Green QD/Siloxane resin (left) and green TSE-QD (right). (b) Yellow QD/Siloxane resin (left) and yellow TSE-QD (right). [8]

Combining the blue LED and optimized yellow TSE-QD, we obtained a natural white, for which the color coordinates of Red TSE-QD (0.702, 0.287), Green TSE-QD (0.265, 0.715), blue LED (0.153, 0.023), and TSE-QD base white LED (0.315, 0.323) occur in the Commission Internationale de l'Eclairage (CIE) 1931 color space (Fig. 5a). To verify the potential for their use for On-Chip type applications, TSE-QD was directly encapsulated in a blue LED chip. The inset photographs in Fig. 4a show red, green, and yellow TSE-QD encapsulated within the blue LED chip. They cover the 116 % color gamut of the National Television Systems Committee (NTSC), as shown by the blue dotted triangle (NTSC) and black solid lined triangle (TSE-QD-based white LED) in Fig. 4a. The TSE-QD-based white LED shows 5410 K of correlated color temperature (CCT) and 72 on the color rendering index (CRI).

To confirm the reliability of the TSE-QD-based white LED, we investigated change in its optical properties under high temperature (85 ℃) and high humidity (85 % RH) condition. As shown in Fig. 4a, the color coordinate of the TSE-QD-based white LED was almost unchanged after aging. Following the stable color coordinates, the PL spectra also showed similar tendencies, in which the PL intensity did not decrease after aging (Fig. 4b). On the basis of our results, we found that our TSE-QD has great potential for use as a luminescent LED encapsulation material for On-Chip type applications.

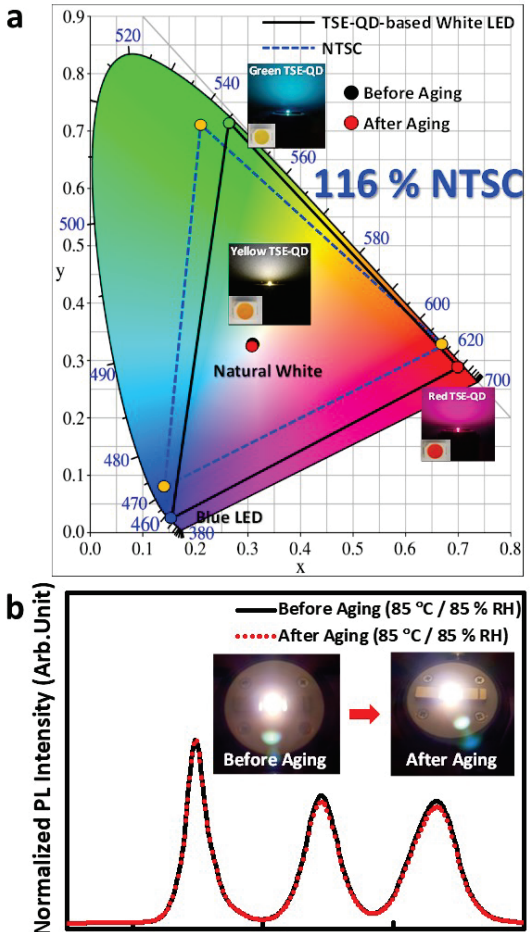

Fig. 3. Optical properties of TSE-QD based white LED
(a) CIE color coordinates of Blue LED, red TES-QD, Green TSE-QD, and TSE-QD-based white LED. (b) PL intensity before and after reliability test at 85 ℃/ 85 % RH. [8]

References

[1] E. Jang, S. Jun, H. Jang, J. Lim, B. Kim, and Y. Kim, "White-light-emitting diodes with quantum dot color converters for display backlights," Adv. Mater., Vol. 22, No. 28, pp. 3076-3080 (2010).

[2] H. Y. Kim, D.-E. Yoon, J. Jang, D. Lee, G.-M. Choi, J. H. Chang, J. Y. Lee, Doh C. Lee, and B.-S. Bae,

"Quantum Dot/Siloxane Composite Film Exceptionally Stable against Oxidation under Heat and Moisture," J. Am. Chem. Soc., Vol. 138, No. 50, pp. 16478-16485 (2016).

[3] H. Y. Kim, D.-E. Yoon, J. Jang, G.-M. Choi, Doh C. Lee, and B.-S. Bae, "Heat-and water-proof quantum dot/siloxane composite film: Effect of quantum dot–siloxane linkage," J. Soc. Infor. Display, Vol. 25, No. 2, pp. 108-116 (2017).

[4] J.-Y. Bae, Y. H. Kim, H. Y. Kim, Y.-W. Lim, and B.-S. Bae, "Sol–gel synthesized linear oligosiloxane-based hybrid material for a thermally-resistant light emitting diode (LED) encapsulant," RSC Adv., Vol. 3, No. 23, pp. 8871-8877 (2013).

[5] J.-S. Kim, S. Yang, and B.-S. Bae, "Thermally stable transparent sol− gel based siloxane hybrid material with high refractive index for light emitting diode (LED) encapsulation," Chem. Mater., Vol. 22, No. 11, pp. 3549-3555 (2010).

[6] J.-Y. Bae, J. Jang, and B.-S. Bae, "Transparent, thermally stable methyl siloxane hybrid materials using sol-gel synthesized vinyl-methyl oligosiloxane resin," J. Sol-Gel Sci. Technol., Vol. 82, No. 1, pp. 253-260 (2017).

[7] S. K. Kuk, J. Jang, H. J. Han, E. Lee, H. Oh, H. Y. Kim, J Jang, K. T. Lee, H. Lee, Y. S. Jung, C. B. Park, and B.-S. Bae, "Siloxane-Encapsulated Upconversion Nanoparticles Hybrid Composite with Highly Stable Photoluminescence against Heat and Moisture," ACS Appl. Mater. Interfaces, Vol. 11, No. 17, pp. 15952-15959 (2019).

[8] J. Jang, D.E. Yoon, S.-M. Kang, Y. H. Kim, I. Lee, H. Lee, Y. H. Kim, Doh C. Lee, and B.-S. Bae, "Exceptionally Stable Quantum Dot/Siloxane Hybrid Encapsulation Material for White Light-Emitting Diode with Wide Color Gamut," Nanoscale, Vol. 11, pp. 14887-14895 (2019).