

Enhancing performance of quantum dot-based light emitting diodes by using poly(methyl methacrylate)@quantum dot hybrid particles

Hyun Chang Kim^{*,‡}, Cheolsang Yoon^{*}, Young-Geon Song^{*}, Young-Joo Kim^{**}, and Kangtaek Lee^{*,†}

^{*}Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul 120-749, Korea

^{**}Department of Mechanical Engineering, Yonsei University, Seoul 120-749, Korea

(Received 27 November 2014 • accepted 6 January 2015)

Abstract—Quantum dots (QDs) are attractive alternatives for organic phosphors in light emitting diodes (LEDs) due to their high quantum yield and photostability. Various methods have been developed for fabrication of LEDs using QDs, yet the reduction in quantum yield during film formation still limits their practical applications. We prepared hybrid particles by coating spherical poly(methyl methacrylate) (PMMA) particles with the CdSe/ZnS QDs, and dispersed them in the PMMA matrix. The PMMA particles were derived from the same material as the PMMA matrix, so that they could not only act as a spacer but also match the refractive index between the polymer particles and matrix. The PMMA@QD hybrid particles exhibited higher quantum yield in both suspension and film states than the pristine QDs. In addition, the dispersion state of QDs in PMMA matrix was significantly improved by using the hybrid particles. Finally, it was demonstrated that the QD-based LED device containing the PMMA@QD hybrid particles exhibited enhancement in both color conversion and luminous efficiencies.

Keywords: Quantum Dot, Light Emitting Diode, Poly(methyl methacrylate), Hybrid Particles, Dispersion

INTRODUCTION

Semiconductor nanocrystals, or quantum dots (QDs), have been a center of research in various applications ranging from photovoltaic to biomedical applications due to their unique characteristics [1-4]. One of the key characteristics that make the QDs such attractive materials is the high photostability (i.e., low photobleaching) compared to organic fluorescent materials. CdSe/ZnS QDs have a lifetime that is approximately 1,000 times longer than typical organic phosphors [5].

Light emitting diode (LED) fabricated with the QDs is one of the most promising research areas in which successful transition from academic research to industrial products is possible. Since their discovery, the QDs have been expected to serve as future display materials because they exhibit broad absorption and narrow emission bands which can be tuned by controlling their size. These characteristics of the QDs are useful in creating a wide range of vivid colors, which cannot be achieved with their organic counterparts. Currently, two approaches are mainly used in fabrication of the QD-based LED devices: electroluminescence and photoluminescence. In the electroluminescence approach, the QDs dispersed in conductive matrix are usually placed between two electrodes [7,8]. On the other hand, the photoluminescence approach places

the film containing red and green QDs on a blue LED that acts as a source of both blue light and excitation light for red and green QDs [9].

One of the hurdles in fabrication of the QD-based LED is an undesirable reduction of quantum yield (QY) during the film preparation step [10,11]. In our previous work, we showed that the QY of QD suspensions (~80%) decreased to 10-20% after film formation [12]. To enhance QY in the film state, we attempted to improve dispersion state of QDs by using the hybrid particles (i.e., QD-coated silica particles), or by surface functionalization with hydrophobic ligands, which could increase the QY by 240% [12,13]. One drawback of the hybrid particles, though, was the refractive index mismatch between the silica particles and poly(dimethylsiloxane) (PDMS) matrix, which decreased the QY due to light scattering.

Herein we have prepared hybrid particles by coating the spherical poly(methyl methacrylate) (PMMA) particles with the CdSe/ZnS QDs, and dispersed them in the PMMA matrix. The PMMA was selected for the polymer matrix because of its superior optical and mechanical properties [14]. Note that the same material as the polymer matrix was used for the synthesis of polymer particles to minimize light scattering from the refractive index mismatch. The dispersion state of QDs in the PMMA film and the performance of the QD-based LEDs were then compared for the PMMA@QD hybrid particles and pristine QDs.

EXPERIMENTAL

1. Materials

We purchased 2,2'-azobis(2-methylpropionamide) dihydrochloride (AIBA, 97%), methyl methacrylate (MMA, 99%), poly(methyl methacrylate) (PMMA, MW: 15 K), polyvinylpyrrolidone (PVP,

[†]To whom correspondence should be addressed.

E-mail: ktleee@yonsei.ac.kr

[‡]Present address: School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA

^{*}This paper is dedicated to Professor Hwayong Kim on the occasion of his retirement from Seoul National University.

Copyright by The Korean Institute of Chemical Engineers.

MW: 10 K), ethylene glycol dimethacrylate (EGDMA, 98%), and tetrahydrofuran (THF, 99.9%) from Aldrich (Yongin, Korea), and 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%) from Junsei Chemical (Tokyo, Japan). Red-emitting oleic acid-capped CdSe/ZnS core-shell QDs were purchased from Nanosquare Inc. (Seoul, Korea).

2. Synthesis of the Hybrid Particles

PMMA particles were prepared by modifying the dispersion polymerization method developed by Peng et al. [15]. Here, AIBA was selected as an initiator to modify the surface of the PMMA particles with amine groups. Briefly, 0.15 g of AIBA and 0.5 g of PVP were added to 100 mL of DI water and the mixture was heated to 70 °C under nitrogen controlled environment. We added 10 g of MMA to the mixture, which turned milky-white after ~150 s. Then, 200 μ L of EGDMA was added as a cross-linker and it was reacted for 24 h. The synthesized PMMA particles were first dispersed in DI water, and then in THF by dialysis. The final concentration of the PMMA particles was set to 22 wt%.

Before the PMMA particles were coated with CdSe/ZnS QDs, they were repeatedly washed using 2-propanol to remove the remaining PVP. Then, 600 μ L of 18.7 μ M QDs dispersed in THF was added to 1.4 mL of the PMMA particle suspension. After 30 min, the hybrid particles were collected via centrifugation and redispersion in THF for analysis. Absence of fluorescence in supernatant after centrifugation confirmed that all the QDs were coated onto the PMMA particle surface.

3. Fabrication of QD/PMMA Films and QD-based LED Devices

QD/PMMA films were fabricated by adding 0.24 g of PMMA to 900 μ L of 11.1 μ M suspension containing either pristine QDs or hybrid particles in MMA, which was then mixed with 100 μ L MMA containing 4 mg of AIBN. This mixture was coated on the glass substrate by spin coating at 4,000 rpm for 90 s, and cured at 50 °C for 2 h. The QD concentration in the resulting QD/PMMA films was 10 μ M. For fabrication of LED devices, the above mixture was dispensed on the blue 5050 SMD type blue emitting LED chip ($\lambda_{\text{ex}}=430$ nm), and cured at 50 °C for 2 h.

4. Characterization

The average hydrodynamic diameter of the hybrid particles was measured by dynamic light scattering (DLS, Malvern Nano-ZS) at room temperature with 4 mW He-Ne laser operating at 633 nm and backscattering angle of 173°. Transmission electron microscopy (TEM, JEOL JEM-2010 at 200 kV) was used to observe the morphology of the hybrid particles. To prepare TEM samples, PMMA@QD particles in THF were air-dried for 24 h, followed by deposition on the Formvar-coated 400 mesh copper grid. Confocal laser microscopy (Carl Zeiss, LSM 510 META) was used to visualize the three-dimensional dispersion state of the QDs in films. The QY of suspensions and films was estimated by using an integrating sphere (Otsuka Electronics) with 405 nm blue laser as excitation energy source. Integrating sphere was also used for LED characterization with 40 mA forward bias current.

RESULTS AND DISCUSSION

1. Fabrication of PMMA@QD Hybrid Particles

Fig. 1 shows the TEM image of the PMMA@QD hybrid particles, which confirms that the spherical PMMA particles are coated

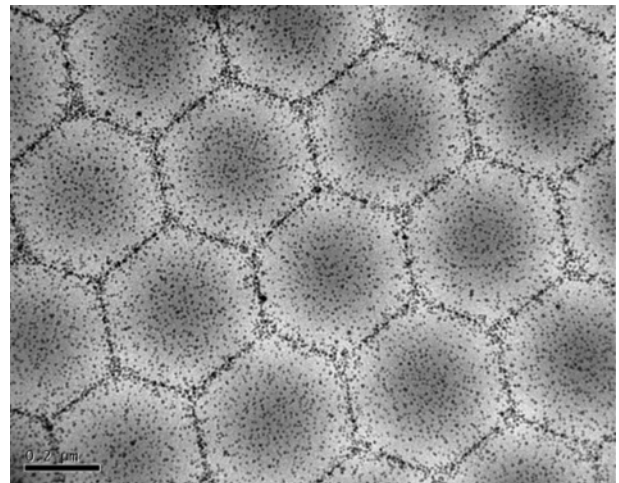


Fig. 1. TEM image of the PMMA@QD hybrid particles.

with the CdSe/ZnS QDs. For dispersion of these particles in solvent before film formation, solvent was selected as follows. Due to the surfactant-aided synthesis of PMMA particles and highly positive zeta potential value (+35 mV), PMMA requires a polar solvent with high dipole momentum for dispersion. On the other hand, the QDs stabilized with oleic acid are usually dispersed in non-polar or polar aprotic solvents with relatively low dipole momentum. Since THF has a mid-range dipole momentum of 1.75, it was chosen as a solvent to disperse the PMMA@QD hybrid particles.

Cross-linked PMMA particles are known to undergo swelling when they are dispersed in good solvents, which can change their refractive index [15]. Refractive index of the swollen particles (n_{mix}) can be estimated using the Lorentz-Lorenz equation in Eq. (1), where n denotes the refractive index, ϕ the volume fraction, 1 the particle, and 2 the solvent [16].

$$\frac{n_{\text{mix}}^2 - 1}{n_{\text{mix}}^2 + 2} = \phi_1 \frac{n_1^2 - 1}{n_1^2 + 2} + \phi_2 \frac{n_2^2 - 1}{n_2^2 + 2} \quad (1)$$

It is easily seen that the Lorentz-Lorenz equation has a first-order linear relationship with the volume fraction, which was experimentally confirmed by Heller [16]. To estimate refractive index of the swollen particles, we applied the Lorentz-Lorenz equation by assuming that cross-linked polymers would swell in good solvents, retaining a spherical shape due to chemical cross-linkages. Since the average diameter of our PMMA particles changed from 306 nm

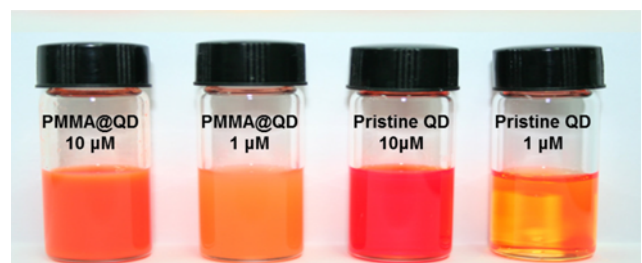


Fig. 2. Photographs of suspensions in THF at different concentrations. From the left, PMMA@QD at 10 μ M, PMMA@QD at 1 μ M, pristine QD at 10 μ M, and pristine QD at 1 μ M.

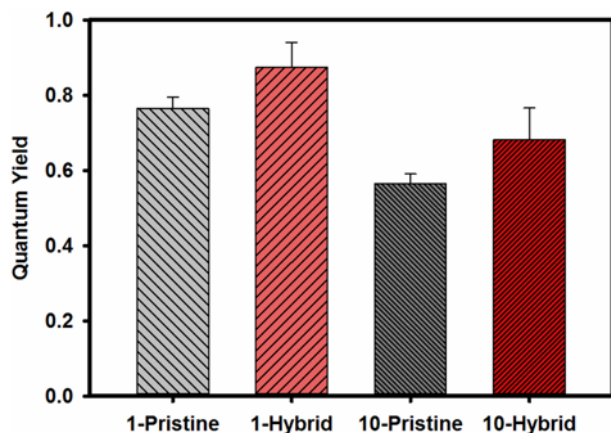


Fig. 3. QY of the suspensions containing the pristine QDs and PMMA@QD hybrid particles in THF. Hybrid and pristine denote PMMA@QD hybrid particles and pristine QDs, and 10 and 1 denote the concentrations of QDs in μM .

to 410 nm after swelling, we could calculate the volume fraction of polymer (ϕ_1) and solvent (ϕ_2) in the swollen particles by assuming spherical particles. As a result, our swollen PMMA particles in THF were found to have a refractive index of 1.441. Fig. 2 shows the pristine QD and the hybrid particle suspensions in THF at two different concentrations. The PMMA@QD hybrid particle suspension was opaque compared to the pristine QDs due to refractive index mismatch between the swollen PMMA particles and THF ($n=1.407$).

2. Quantum Yield of Pristine QD and Hybrid Particle Suspensions

Fig. 3 compares the QY of the pristine QDs and PMMA@QD hybrid particles in THF at two different concentrations, 1 μM and 10 μM . At both concentrations, the PMMA@QD hybrid particles show higher QY than the pristine QDs. It is well known that fluorescence quenching and reduction in QY occur due to electronic coupling and energy transfer when the QDs are in the close proximity [17]. Therefore, we suspect that PMMA particles in the hybrid particles acted as a spacer to increase the average inter-dot distance between QDs, thereby increasing the QY in suspension. Moreover, it is possible to calculate the distance between the pristine QDs in suspension using Eq. (2) [18]:

$$D = \sqrt[3]{\frac{6(V_{QD} + V_S)}{\pi N_{QD}}} \quad (2)$$

where V_{QD} is the volume occupied by the QDs, V_S the volume of the solvent used, and N_{QD} the total number of the QDs. From Eq. (2), the distance between the pristine QDs at 1 μM and 10 μM was found to be 147 nm and 68 nm, respectively, which confirms longer inter-dot distance at lower concentration (1 μM) and hence the higher QY as shown in Fig. 3.

3. Quantum Yield of QD/PMMA Films and LED Devices

QDs dispersed in polymer films always exhibit significant reduction in QY due to aggregation of QDs. It is believed that the small size and low affinity of QDs to PMMA are responsible for aggregation of QDs. By using the PMMA@QD hybrid particles, we expect enhancement in the dispersion state because the PMMA particles

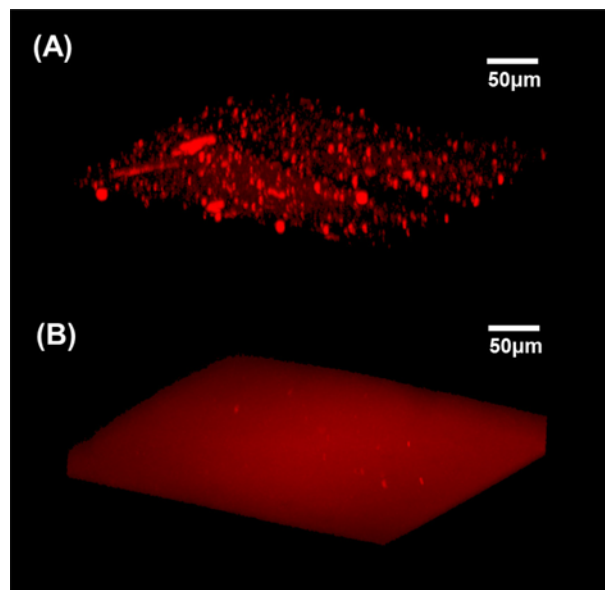


Fig. 4. Three-dimensional confocal images of the QD/PMMA films with (A) pristine QDs and (B) PMMA@QD hybrid particles.

could act as a spacer and there should also exist favorable interaction between the PMMA particles and matrix. We analyzed the three-dimensional dispersion state of QDs in the PMMA matrix using confocal laser microscopy. Combining multiple image stacks taken at different focal planes allowed us to visualize the exact location of the fluorescent materials in the matrix. Fig. 4 clearly shows that the pristine QDs were seriously aggregated, whereas the PMMA@QD hybrid particles were evenly distributed in the PMMA matrix. This confirms that the dispersion state of QDs was significantly enhanced by using the PMMA@QD hybrid particles. As a result of the enhanced dispersion, the hybrid particles showed the increase in QY up to ~40% as shown in Fig. 5. If we consider the initial QY in suspension (~68%), the reduction in QY during film fabrication process was only 28% with the hybrid particles.

Finally, we tested the possibility of using these particles in fabrication of the QD-based LED device. Fig. 6 shows the electrolumi-

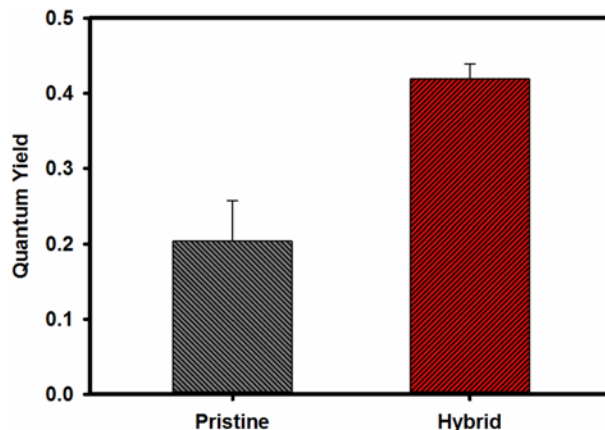


Fig. 5. QY of the pristine QDs and PMMA@QD hybrid particles dispersed in PMMA matrix at 10 μM .

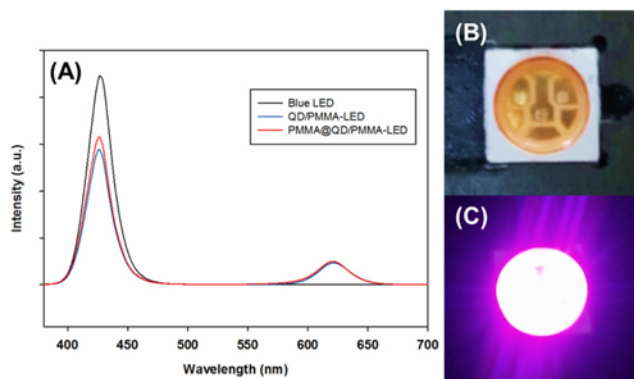


Fig. 6. (A) EL emission spectra of different types of LED devices. Photographs of (B) the as-fabricated LED device with the PMMA@QD hybrid particles and (C) the LED operating under 40 mA.

Table 1. Color conversion and luminous efficiencies of the QD-based LEDs prepared with the pristine QDs and PMMA@QD hybrid particles under a 40 mA forward bias current

LED type	Color conversion efficiency (%)	Luminous efficiency (lm W^{-1})
Without QDs	-	19.97
With hybrid particles	49	41.77
With pristine QDs	36	35.24

nescence (EL) emission spectra of the blue-LED and QD-based LED packages. The color conversion and luminous efficiencies of the pristine and hybrid QDs are also summarized in Table 1. Here the color conversion efficiency was defined as the ratio of the converted QD emission to the blue emission spent to convert QD emission in the LED package. Because of better dispersion of the PMMA@QD hybrid particles, which can reduce reabsorption between QDs, color conversion efficiency of the QD-based LED package made with the hybrid particles was found to be higher (49%) than that made with the pristine QDs (36%). In addition, the luminous efficiency of the LED package containing the PMMA@QD-LED hybrid particles was found to be higher (41.77 lm W^{-1}) than that with the pristine QDs (35.24 lm W^{-1}) when the blue-LED with efficiency of 19.97 lm W^{-1} was used under 40 mA forward bias current. We believe that improved dispersion of QDs and similar refractive indices between the PMMA@QD hybrid particles and PMMA matrix reduced light scattering, and hence prevented reduction in luminous efficiency of the QD-packed LED package. Therefore, it should be possible to enhance luminous efficiency of the QD-based LEDs by improving dispersion state of QDs and matching refractive indices between particles and matrix.

CONCLUSIONS

PMMA@QD hybrid particles were prepared and dispersed in PMMA matrix for fabrication of QD-based LED. Using confocal

laser microscopy, we showed that dispersion state of QDs could be improved with the PMMA@QD hybrid particles because the PMMA particles acted as a spacer and a favorable interaction existed between PMMA particles and matrix. Similar enhancements in the color conversion and luminous efficiencies were also observed when the LED device was fabricated with the PMMA@QD hybrid particles compared to the pristine QDs, because light scattering could be reduced from the improved dispersion and refractive index matching. These results suggest a new design protocol to enhance performance of LED devices based on QDs.

ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF) grants (Nos. 2014R1A2A1A11051436, 2009-0082417).

REFERENCES

- V. Gupta, N. Chaudhary, R. Srivastava, G. D. Sharma, R. Bhardwaj and S. Chand, *J. Am. Chem. Soc.*, **133**, 9960 (2011).
- J. Lee, V. C. Sundar, J. R. Heine, M. G. Bawendi and K. F. Jensen, *Adv. Mater.*, **12**, 1102 (2000).
- C. Wu, B. Bull, C. Szymanski, K. Christensen and J. McNeill, *ACS Nano*, **2**, 2415 (2008).
- T. Kang, H. C. Kim, S. W. Joo, S. Y. Lee, I. S. Ahn, K. A. Yoon and K. Lee, *Sens. Actuators, B Chem.*, **188**, 729 (2013).
- J. R. Lakowicz, *Principles of fluorescence spectroscopy*, Springer US, New York (2006).
- B. O. Dabbousi, J. Rodriguez-Viejo, F. V. Mikulec, J. R. Heine, H. Mattoussi, R. Ober, K. F. Jensen and M. G. Bawendi, *J. Phys. Chem. B*, **101**, 9463 (1997).
- S. Coe, W. K. Woo, M. Bawendi and V. Bulovic, *Nature*, **420**, 800 (2002).
- B. O. Dabbousi, M. G. Bawendi, O. Onitsuka and M. F. Rubner, *Appl. Phys. Lett.*, **66**, 1316 (1995).
- H. S. Jang, H. Yang, S. W. Kim, J. Y. Han, S. G. Lee and D. Y. Jeon, *Adv. Mater.*, **20**, 2696 (2008).
- D. Qi, M. Fischbein, M. Drndić and S. Šelmić, *Appl. Phys. Lett.*, **86**, 093103 (2005).
- D. E. Fogg, L. H. Radzilowski, B. O. Dabbousi, R. R. Schrock, E. L. Thomas and M. G. Bawendi, *Macromolecules*, **30**, 8433 (1997).
- H. C. Kim, H.-G. Hong, C. Yoon, H. Choi, I.-S. Ahn, D. C. Lee, Y.-J. Kim and K. Lee, *J. Colloid Interface Sci.*, **393**, 74 (2013).
- C. Yoon, H. G. Hong, H. C. Kim, D. Hwang, D. C. Lee, C. K. Kim, Y. J. Kim and K. Lee, *Colloids Surf., A*, **428**, 86 (2013).
- H. M. Zidan and M. Abu-Elnader, *Phys. B*, **355**, 308 (2005).
- B. Peng, E. van der Wee, A. Imhof and A. van Blaaderen, *Langmuir*, **28**, 6776 (2012).
- W. Heller, *Phys. Rev.*, **68**, 5 (1945).
- R. Koole, P. Liljeroth, C. D. Donega, D. Vanmaekelbergh and A. Meijerink, *J. Am. Chem. Soc.*, **128**, 10436 (2006).
- K. Tai, W. Lu, I. Umezu and A. Sugimura, *Appl. Phys. Express*, **3**, 035202 (2010).