Light Conversion Efficiency Enhancement of Modified Quantum Dot Films Integrated With Micro SiO_2 Particles

Yongming Zhu, Wei Chen, Jinyan Hu, Bin Xie, Junjie Hao, Dan Wu, Xiaobing Luo, and Kai Wang

***Abstract*—Photoluminescence quantum dots (QDs) have been considered as a kind of promising light converting materials with high luminous efficiency, tunable spectrum, and narrow emission. However, the current light conversion efficiency (LCE) of QD films is at a relative low level, which will result in many problems, such as inferior luminous performance, severe self-heating, etc. To enhance the LCE of QD films, SiO2 particles were doped into QD films by physical blending, for their remarkable light scattering effect. The LCE enhancement after adding SiO2 particles were studied by experiments. Experimental results showed that the SiO2 modified QD films improved the LCE up to 63.45%, which was 103.88% higher than conventional QD films. Besides, as the SiO2 particles diameters increased, the optimal mass fractions of SiO2 particles for top LCE would decrease.**

***Index Terms*—Films, light conversion efficiency (LCE), quantum dots (QD), scattering, SiO2.**

I. Introduction

PHOTOLUMINESCENCE quantum dots (QDs) have been considered as a promising light converting materials for display and lighting applications [1]–[4]. Compared with organic light-emitting diodes, QDs are emerging as a cost-effective solution to the next generation of display and solid-state lighting which demands superior performance in efficiency, brightness, color saturation and color rendering index [1], [5], [6].

In recent years, a kind of CdSe QDs has been obtained. It shows high fluorescence quantum yield and narrow emission with full width half maximum of 20-30 nm. Hao *et al*. [7] demonstrated a tri-n-octylphosphine-assisted successive ionic layer adsorption and reaction method to synthesize CdSe-ZnS core-shell QDs with quantum yield of 95%. QD film is a common pattern to package QDs that dispersing the QDs particle within matrix film [8], [9]. However, the light conversion efficiency (LCE) of QD film was at a relative low level during preparation and packaging. A large portion of light would be transferred into heat [10], [11]. Unfortunately, the thermal conductivity of polymer matrix is too low to abstract the heat out of the film and further lead temperature rising [12], [13]. This situation would deteriorate the films reliability due to QDs' temperature sensitivity [14], [15]. However, there are few articles aiming at the LCE of QD film, and the only method to improve the LCE is to adjust the packaging structure of QD films. Woo *et al*. [16] developed layered QD-phosphor based LEDs and optimized the mounting sequence of QDs and phosphors films. Due to the low LCE of QDs films (about 50%), the maximum luminous efficiency was only 71.2 lm/W.

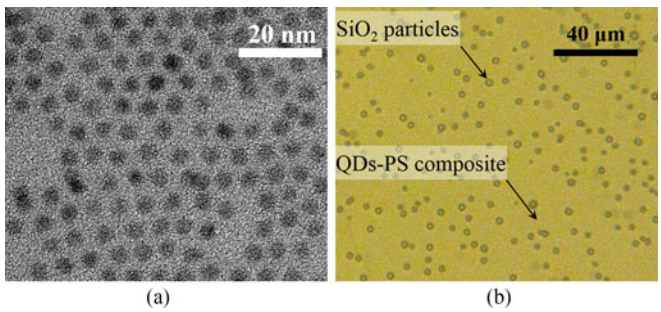

Fig. 1. (a) High resolution TEM image of QDs dispersed uniformly in chloroform solution. (b) Photomicrograph of MQDF blended with 2 μm SiO_2, in which the granules are SiO_2 particles and the matrix is the composite of QDs and PS.

In white LED packaging, SiO_2 particles are adopted to improve the LCE of the phosphor silicone composites, benefiting from the scattering effect, refractive index and crystal structure of SiO_2 particles [17]–[19]. Nevertheless, there is still no relative literature referring to the LCE enhancement of QDs films by blending SiO_2 particles.

In this study, QD films were manufactured by blending high quality QDs into polystyrene (PS) matrix physically in advance. By contrast, SiO_2 particles were doped into the QD-PS composite to obtain modified QD films (MQDFs). The influence of SiO_2 particles mass fractions and diameters upon LCE was investigated by experiments. In addition, the mechanism of LCE enhancement by SiO_2 was also analyzed.

II. Experiments

Fig. 1(a) shows the transmission electron microscope (TEM) image of QDs which are dispersed uniformly in chloroform solution. The CdSe/CdS/ZnS QDs solution used in this study

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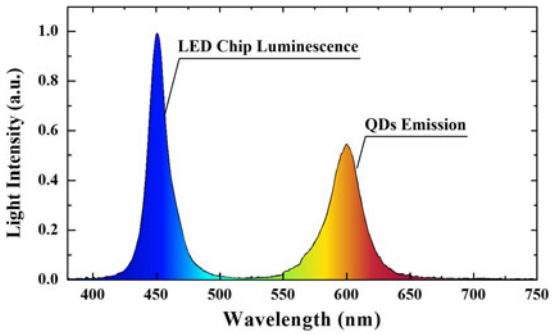

Fig. 2. Luminescence spectra of QD films illuminated by a blue InGaN chip under driving current of 50 mA.

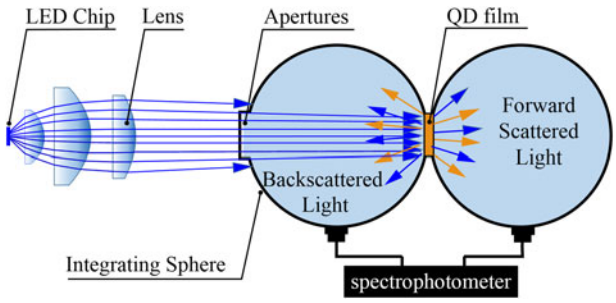

Fig. 3. Schematic diagram of double integrating spheres system.

was synthetized based on the previous work [7], [21]. The photoluminescence quantum yield reach up to 80%. The MQDF preparation contains 6 steps: 1) 1.0 g PS was completely dissolved into 2.0 ml chloroform; 2) 0.25 ml CdSe/CdS/ZnS QDs chloroform solution with the absorption of 0.34 after diluting for 100 times was blended thoroughly with the above PS-chloroform solution; 3) SiO_2 particles were hydrolyzed by a spot of alcohol and diluted by chloroform and blended with the above QDs-PS-chloroform composite thoroughly; 4) the air bubbles in the mixture were removed by ultrasonic treatment; 5) the mixture was poured cautiously into a glass container with 60 mm diameter; 6) the MQDF was molded after the solution volatilized with the protection of N_2 for 48 h. The thickness of obtained MQDF is 0.4 mm and present high consistency. Fig. 1(b) shows the photomicrograph of an MQDF with 2 μm dispersed SiO_2. Fig. 2 shows the luminescence spectra of QD films illuminated by a blue InGaN chip (50 mA driving current). From this figure, it was indicated that the emission peak wavelength of the QDs was about 595 nm, whose emission characteristics are free from the SiO_2 particles.

A double integrating spheres system with a parallel incident light source was applied to measure and calculate the LCE of the prepared films. It was illustrated in Fig. 3. To avoid the potential test errors by divergent incident light, three convex lenses were used to collimate the incident light. A spectrophotometer was used to test the forward-scattered and backscattered light spectra. Based on the previous work [22], [23], the LCE of the

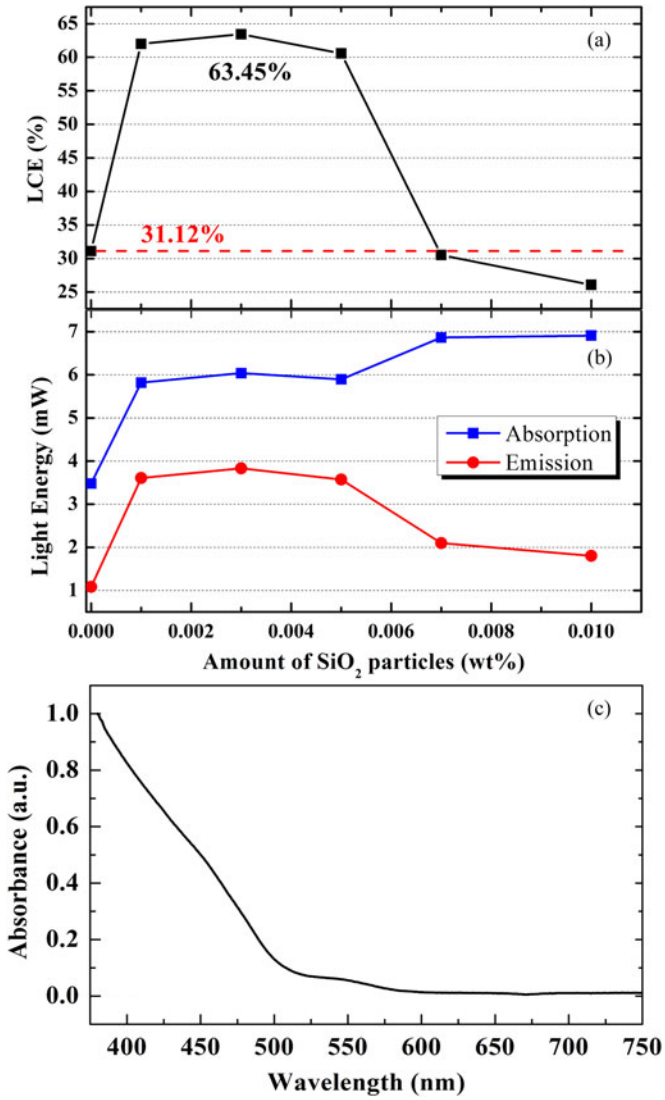

Fig. 4. (a) The LCE of MQDFs and (b) the absorption of blue light and the emission of yellow light of MQDFs with different mass fractions of 8 μm SiO_2 particles. (c) The absorption spectra of CdSe/CdS/ZnS QDs.

composite films can be calculated by

$$\eta_{\mathrm{LCE}} = \frac{P_y}{P_{\mathrm{total}} - P_b}. \tag{1}$$

P_{total} denotes the total power of the blue light from LED chip with 454 nm emission peak. P_b denotes the power of the transmitted blue light added up with the reflected blue light measured by two integrating spheres separately. Thus, the absorption of blue light was denoted as $P_{\mathrm{total}} - P_b$. P_y denotes the total power of yellow light.

III. Results and Discussion

To search for the optimal mass fraction of SiO_2 particles, we increased the quantity of SiO_2 gradually with diameter of 8 μm in Step 3. Fig. 4(a) displays the MQDF LCE with different SiO_2 particles mass fractions. It was verified from the experimental

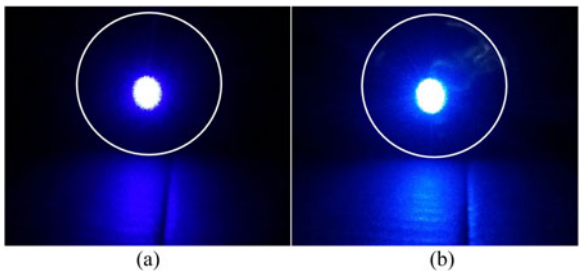

Fig. 5. Images of PS films illuminated by collimated parallel light from blue LED chip, the white circles indicated the outline of PS films. (a) Light spot on pure PS film and (b) on PS film with 0.01% SiO_2 particles under diameter of 8 μm.

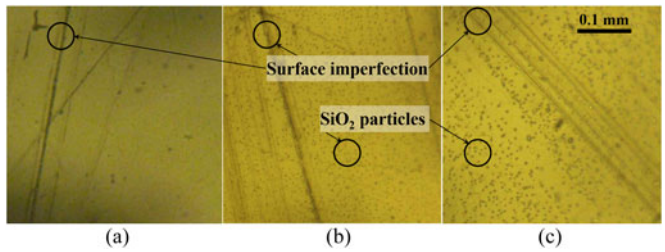

Fig. 6. Surface imperfection images of (a) pure PS film, (b) film with 2 μm SiO_2 particles and (c) film with 8 μm SiO_2 particles.

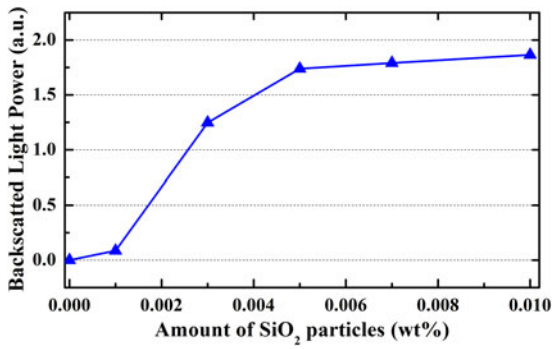

Fig. 7. Backscattered light energy of MQDFs with the increasing mass fractions of SiO_2 particles.

results that the peak value of LCE was 63.45% at 0.003 wt%, higher than the QD films without SiO_2 by 103.88%. As the mass fraction increased to 0.007%, the LCE reduced to 30.52%, less than the QD films without SiO_2. To explicate the physical mechanism behind the phenomena, the blue light absorption and the yellow light emission of MQDFs were tested and illustrated in Fig. 4(b). It was noticed that as the fractions of SiO_2 increased, the absorption of blue light increased monotonously, while for the emission of yellow light, there was an emission peak on the mass fraction of 0.003% approximately. These phenomena could be understood as follow: 1) owing to the strong scattering effect of SiO_2 particles, the blue light absorption was enhanced because of the increased optical distance through the MQDF, and the yellow light emission was enhanced correspondingly because of more blue light was transferred by QDs; 2) the emitted yellow light would have more chance to be extracted from the films, because it is much more likely to avoid the total internal reflection of the films after being scattered by SiO_2 particles; and 3) the absorption spectra of CdSe/CdS/ZnS QDs was illustrated in Fig. 4(c), from which it can be seen that part of the emission light with wavelength of 550∼600 nm will be reabsorbed by QDs. So with the increase of mass fraction of SiO_2 particles, the yellow light emitted out from CdSe/CdS/ZnS QDs would have more chance to be scattered by SiO_2 particles, and it will increase the optical path of yellow light in the QD film and the probability of self-absorption by QDs, which will result in the light energy decreasing of the yellow light.

Contrast experiments were conducted to investigate the SiO_2 scattering effect on the variation trend of LCE. PS films containing no QDs were fabricated by adding different quantity of SiO_2 particles with diameters of 8 μm into the PS-chloroform. Fig. 5 shows the illumination comparison between the PS films with 0.01% SiO_2 particles and the pure PS film. Because of the scattering effect, the light spot on PS film with SiO_2 particles was more emanative than the latter. To characterize the effect of SiO_2 particles, backscattered light energy was introduced below:

$$P_{\mathrm{BS}} = P_B - P_{B0} \tag{2}$$

where P_B denotes the backward light energy of the composite films with SiO_2 particles. P_{B0} denotes the backward light energy of the composite films without SiO_2 particles. To study the influence of SiO_2 particles on the optical characteristics of the films interface, the microscope tests were conducted. Fig. 6 shows the surface imperfection images of pure PS film, film with 2 μm SiO_2 particles and film with 8 μm SiO_2 particles. The backscattered light energy with different SiO_2 mass fraction was tested and illustrated in Fig. 7. It was found that as the SiO_2 mass fraction increases, the backscattered light energy increases monotonously and the scattering effect is enhanced. Fig. 7 can well explain that more yellow light is emitted from the excited QDs particles as Fig. 4(b) shows. Nevertheless, when the dosage of SiO_2 exceeded 0.003% in Fig. 4(b), too much yellow light will be reabsorbed by the QDs SiO_2 particles with poor efficiency, so there is a downtrend for the yellow light emission when the mass fraction is larger than 0.003%, which could partly account for the presented variation trend of the LCE shown in Fig. 4(a). Additionally, when the emergence angle of emitted light exceed the total internal reflection angle, the light is unable to escape from the composite films and weakens the LCE. SiO_2 particles could improve this situation. Light get more chances to adjust the emergence angle after several scatterings and cross through the film. As a consequence, the macroscopical LCE of the MQDF was in an upward tendency at the mass fraction below 0.003%.

Fig. 8 shows the LCE variation tendency of MQDFs with the 4 kinds of SiO_2 particles diameter. The SiO_2 dosage at each LCE curve peak are 0.008%, 0.005%, 0.003% and 0.001% for particle diameter of 2, 5, 8 and 10 μm, respectively. Hence, the increase of the particles diameter could reduce the SiO_2 dosage. Fig. 9 shows the mass fraction for peak LCE with different diameters of SiO_2 particles. The demanded dosage of SiO_2 particles for

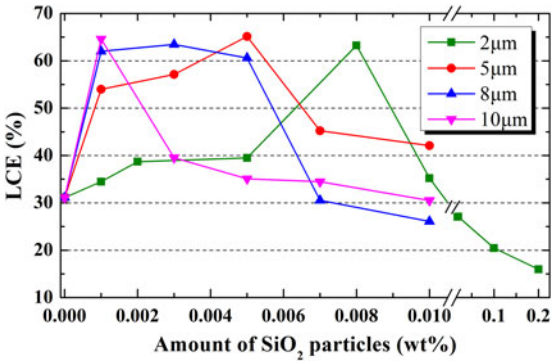

Fig. 8. The LCE variation tendency of MQDFs with the mass fractions of SiO_2 particles in varied diameters.

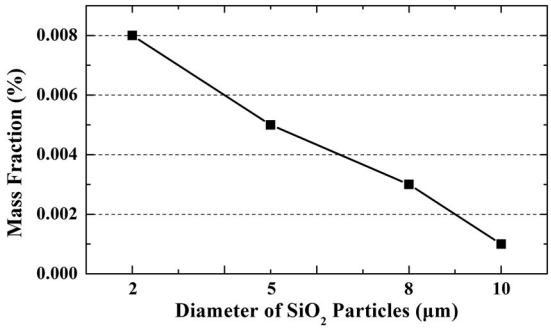

Fig. 9. The mass fraction for LCE peak with diameters of SiO_2 particles.

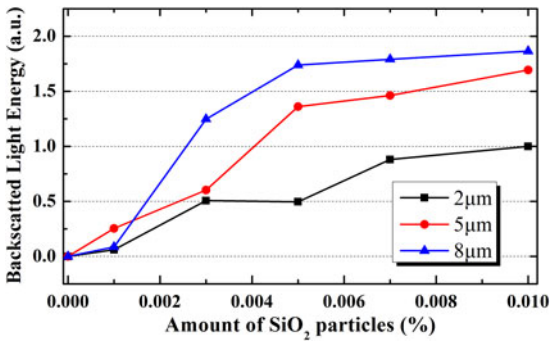

Fig. 10. Backscattered light energy with the mass fractions of SiO_2 particles in varied diameters.

the optimal LCE remained a falling trend with the increasing particles size. Fig. 10 shows the backscattered light energy of different size of SiO_2 with different amount of SiO_2 particles. It could be found that at the same mass fraction, the extent of Mie scattering was enhanced with the increase of particle diameters. In other words, the dosage of larger SiO_2 particles for optimal LCE could be less than that of smaller ones within a certain range.

IV. Conclusion

In this study, SiO_2 particles were added into the QD films by physical blending to enhance the LCE of QD films. The mass fractions and diameters of the particles were investigated by experiments. It could be verified that, due to the strong scattering effect of SiO_2 particles, the LCE of the QD films was substantially enhanced. The maximum enhancement of MQDFs' LCE could reach up to 63.45%. Additionally, the Mie scattering effect of SiO_2 particles with larger sizes was stronger than that of smaller ones at the same mass fraction, the dosage of larger SiO_2 particles for optimal LCE could be less than that of smaller ones within a certain range.

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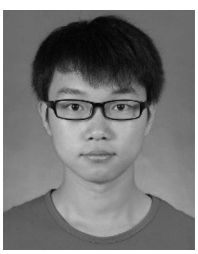

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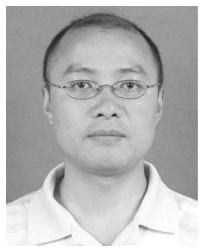

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