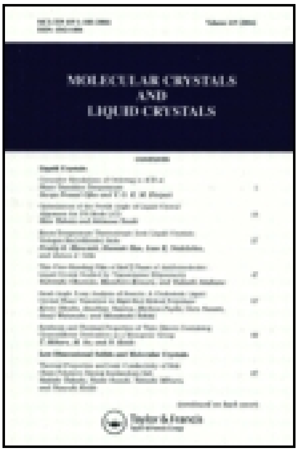
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White LED Packaging with Layered Encapsulation of Quantum Dots and Optical Properties

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The preparation method of encapsulating paste containing YAG phosphor and red quantum dot (QD) in silicone resin and the structure of phosphor layers were studied from the view point of improving both the efficiency and color rendering index (CRI) of the phosphor converted white LED (pcWLED). The addition of red phosphor or red QD in addition to the YAG phosphor could increase CRI of the pcWLED, but the efficiency was decreased. The pcWLED packaged with the encapsulant where the red QD was mixed in advance with the part of the silicone resin and mixed again with the YAG phosphor dispersed the remaining in silicone resin exhibited higher CRI and efficiency than the one packaged with one pot mixture of YAG and red QDs. The pcWLEDs made by silicone encapsulant with YAG phosphor and red QD at the ratio of YAG:QD = 5.0:0.5wt% exhibited that both efficiency and color rendering index could be increased at same time by adopting YAG phosphor and QD encapsulation in a layer-by-layer structure on top of InGaN LED chip.

Keywords Light emitting diode; LED; quantum dot; color rendering index; luminous efficiency

Introduction

The development of white light-emitting diodes (WLEDs) has attracted significant interest for solid-state illumination applications due to their high efficiency, long life, low-power consumption, fast response time and reliability [1,2]. Two types of WLED have been widely studied as alternative for replacing convertional light sourecs. Multichips WLEDs, constructed by a red-, a green-, and a blue-emitting chip, show three emission bands and possess a good color rendering. However, they are expensive and need a relatively complex external detector and feedback system because each chip degrades at a different rate [3].

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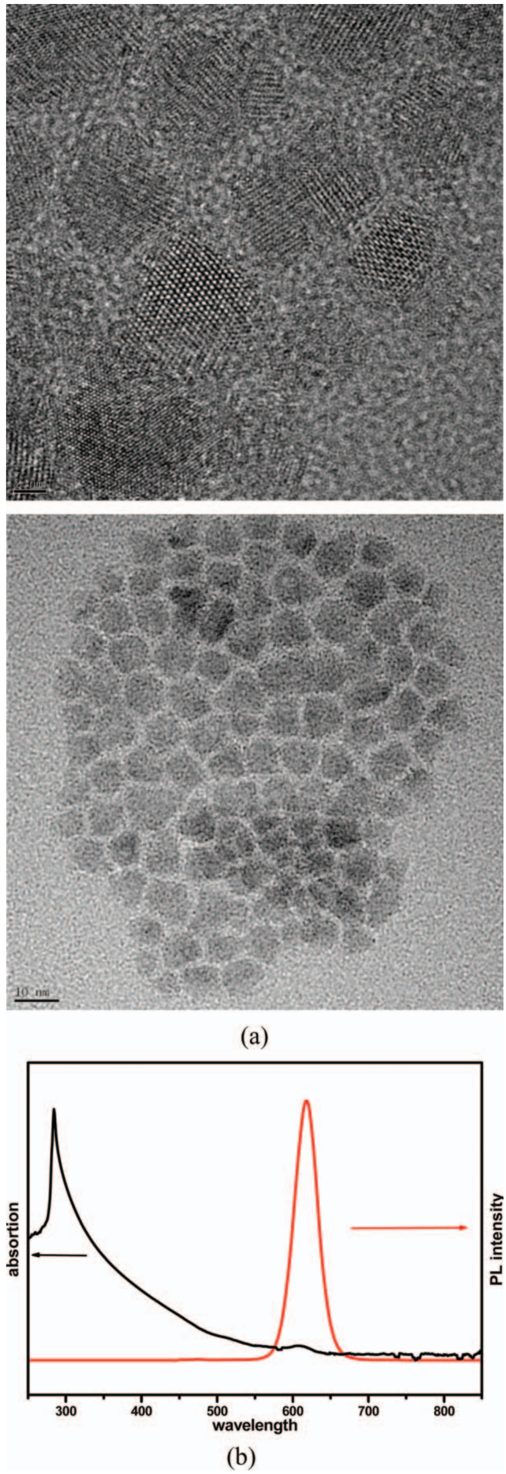

Figure 1. (a) TEM images of CdSe/CdS/ZnS core multishell QD and (b) UV-vis absorption and PL spectra of QD.

Single-chip WLEDs will be used as general lighting in the future due to low cost and high luminescence efficiency. This WLED comprises only a blue InGaN chip and a yellow-emitting yttrium aluminum garnet (YAG) phosphor, so white light is produced by mixing yellow emission from YAG excited by some of the InGaN blue emission, with the remaining InGaN blue light. Typical YAG doped with cerium is most widely used in single-chip WLEDs, however, such source lack red component giving lower color rendering than that of multichips WLEDs [4]. Consequently, some novel phosphors, for example, organic phosphors with flexibly selected emission color and high efficiency have been reported [5,6]. Nevertheless, the instability and long-term reliability of organicmaterials are doubtful.

H.J.Yu et al. fabricated a surface mounted device (SMD) type WLED in which a blue InGaN LED was used as the excitation source and a green-emitting copolymer as organic phosphor. In order to increase the color rendering index (Ra) of the WLED, they incorporated quantum dots in the green-emitting polymer and then used the QD and polymer composite as an encapsulant of InGaN LED chip. They reported WLED with luminous efficiency of 44.2 lm/W and Ra of 75.3 and confirmed the Foester type energy transfer from the green-emitting polymer to the red QDs [7]. White LEDs utilizing QDs have also been fabicated by adopting photosensitive epoxy resin as encapsulating material and curing the QD plus epoxy resin mixture with the blue light coming from the InCaN-based LED chips. It was demonstrated that this packaging method could give WLED by simple process with relatively high (66.20) color rendering index [8]. The effect of stucture of phosphor encapsulation on phosphor converted WLED (pcWLED) was also studied. The new pcWLED had package structure consisted of an inverted cone lens encpsulant and a ring remote phosphor layer. The geometrical configuration of the inverted cone lens increased the phosphor extraction efficiency of the pcWLED by diminishing the backward light from the phosphor layer to the absorptive LED chip [9].

The effect of structural stability of QDs on the performance fo pcLED was also studied from the view point of application to the LED back light of the liquid crystal displays. E. Jang et al. synthesised CdSe//ZnS/CdSZnS green QDs and CdSe/CdS/ZnS/CdSZnS red QDs [10]. After Hines and Guyot-Sionnest reported on the ZnS-capped QDs showing luminescence up to 50% quantum efficiency, considerative efforts were devoted to optimizing QD structures to achieve intense and narrow emissions [11]. However their luminescence efficiencies were easily degraded during the processes of ligand exchange, incororation into solid states, and long-term exposure to photoexitation. These were mainly attributed to the surface traps generated by the detachment of organic passivating ligands, destabilized core/shell interfaces, or the structural changes to the oxide crystals [10]. Although various methods have been proposed for the use of WLED in the solid state lighting, the phosphor converted WLED is the most common method exploited in solid state lighting. Many materials such as inorganic phosphors and organic dyes and light emitting materials have been tested for their application to the phosphor converted WLED, however, QDs have shown great potential for both the next ganeration solid state lighting and high quality back light unit of the LCDs.

This study presents a new package structure for pcWLEDs that utilize layer-by-layer encapsulation of red-emitting CdSe QDs on top of the yttrium aluminium garnet (YAG) phosphor with silicone resin as encapsulating materials. The preparation method of encapsulating paste with YAG phosphor and red QDs and the structure of phosphor layers were examined from the view point of improving both the efficiency and color rendering index of the resulting pcWLEDs at same time.

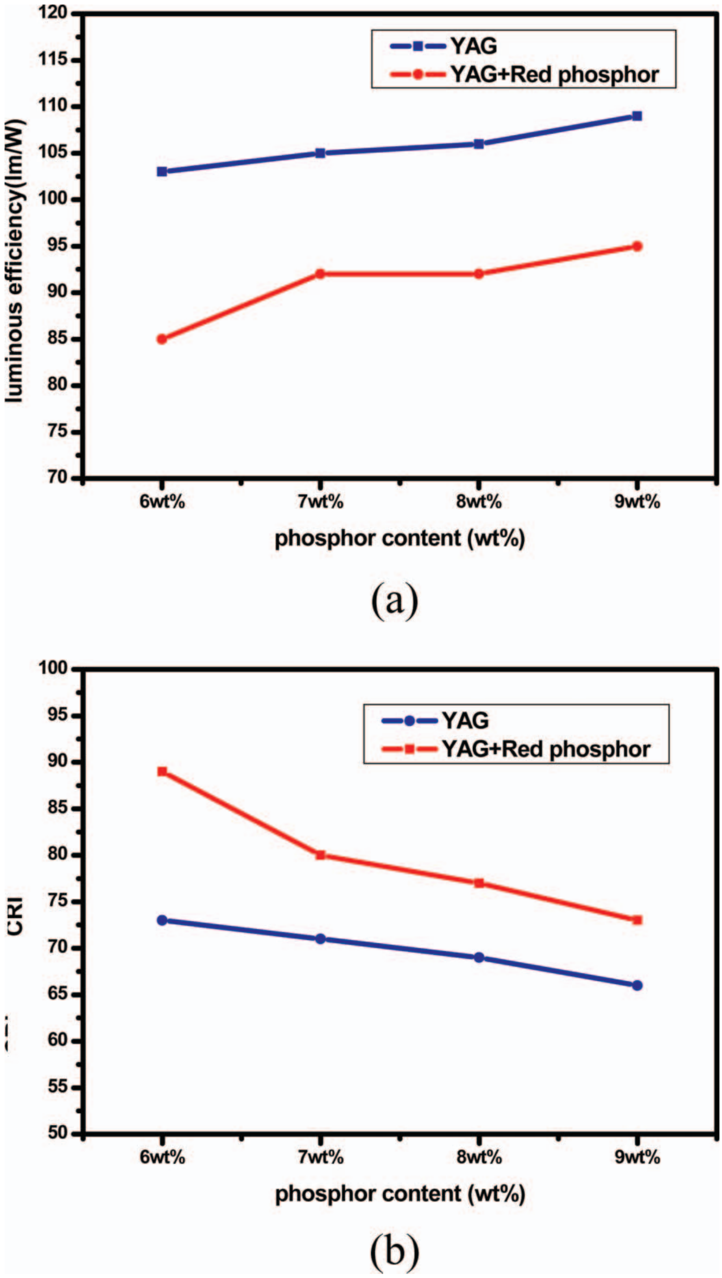

Figure 2. (a) The luminous efficiency and (b) CRI of pcWLEDs made with YAG and YAG plus red phosphor encapsulation.

Experimental

Yellow-emitting Y3Al15O12:Ce3 + (YAG:Ce) phosphor and nitride red phosphor were obtained from Lumimicron Co., in Korea. The 624 nm red-emitting CdSe/CdS/ZnS core–multishell QDs were purchased from QD Solutions Co. (Daejeon, Korea) and used without further purification. The QDs were dispersed in toluene and dropped on 300-mesh perforated carbon grids to prepare the samples. The emission peak and dominant wavelength of LED chip (Cree Co. Ltd.) were 455 nm and 460 nm, respectively. The half width of the emission spectrum of the chip was in the range of 22∼24 nm. The total radiant flux of the chip was in the range of 280∼300 mW@350 mA. The dual component thermally curable silicone resin (OE-6630 A and B) was purchased from Dow Corning. Silver (Ag) epoxy resin used as die adhesive was purchased from Smitomo Co., Japan. UV–vis absorption spectra were measured using a Scinco SD-1000 UV–vis spectrophotometer. PL spectra were recorded using a Horiba Fluorolog spectrometer at room temperature with xenon lamp as the excitation source. Transmission electron microscopy (TEM) images were obtained using an FEI Tecnai G2F30 S-Twin device at 300 kV.

The silicone based encapsulants were made by mixing silicone resin parts A and B in a 1:4 weight ratio in the mixing/degasing machine made by Thinky Co., Japan utilizing YAG phosphor and red QDs. The phosphor containing silicone encapsulant was injected in the LED lead frame by dispensor and then thermally cured in the convection oven for 4hours according to the curing profile. Optical characteristics such as electroluminescence (EL), luminous efficiency, color temperature, Commission Internationale de l Eclairage (CIE) color coordinates and CRI values of the WLEDs were evaluated by using integrating sphere with Leos program.

Rsults and Discussion

Figure 1(a) shows TEM images of CdSe/CdS/ZnS core–multishell QDs and QD solutions under 365 nm ultraviolet (UV) illumination. The CdSe/CdS/ZnS core–multishell QDs appear quite clearly on the TEM grid and exhibit a uniform size distribution without agglomeration. The well-defined lattice fringes for the core–multishell QD particles shown in Fig. 1(a) indicate that core–multishell QDs have a well-defined crystalline structure. The TEM images indicate that the average particle size of red-emitting core–multishell QDs was about 6.5 nm. Figure 1(b) shows typical UV–vis absorption spectra and corresponding PL spectra of core–multishell QDs with emission peak at 624 nm.

We first tried to establish a reference device for phosphor converted WLED utilizing InGaN blue LED with YAG phosphor and YAG plus red phosphor shown in Fig. 1. Here the two powder phosphors were mixed with the silicone resin and encapsulated on top of the InGaN LED chip. The concentration of YAG phosphor in pcWLED was 6–9wt% based on silicone resin and the concentration of the red phosphor in YAG/red phosphor mixture was 1 wt% in addition to the 6–9wt% of the YAG phosphor. The luminous efficiency and color rendering index (CRI) of the pcWLED are shown in Fig. 2. As shown in Fig. 2 the CRI of the white LED was increased by addition of red phosphor, but the decrease of

Table 1. Color coordinates, Tc and Ra of pcWLEDs fabricated with YAG (5wt%) and red QD (0.05wt%) in silicone encapsulation

Device No.	Coordinates (x,y)	Tc(K)	Ra
pcWLED-1	(0.34, 0.37)	4900	64
	(0.34, 0.36)	5000	64
pcWLED-2	(0.33, 0.33)	5500	72
	(0.33, 0.34)	5400	71

Table 2. Color coordinates, CRI(Ra) and efficiency(K) of pcWLED encapsulated with YAG phosphor and QD

Device No.	Coordinates (x, y)	Ra	K (lm/W)
pcWLED-3	(0.29, 0.30)	68	91
pcWLED-4	(0.29, 0.30)	71	80
pcWLED-5	(0.29, 0.30)	73	76

luminous efficiency was observed. This trade-off phenomenon of the pcWLED is ascribed to the absorption of green region light by the red phosphor. A considerable portion of the radiation from the blue LED and red phosphor could not contribute to the luminous efficiency due to the photopic sensitivity of the human eye and also to the efficiency measuring system.

The substitution of red phosphor with red QD's was studied from the view point of improving the efficiency and CRI of the pcWLED at the same time. The effect of mixing YAG phosphor and red QDs instead of red phosphor powder is shown in Table 1. As shown in Table 1 the device pcWLED-2 exhibited higher efficiency and color rendering index. In Table 1 the first device (pcWLED-1) was packaged with the encapsulant in which YAG phosphor and red QD was mixed together with the silicone resin and the pcWLED-2 was packaged with the encapsulant where the red QD was mixed in advance with the part of the silicone resin and mixed again with the YAG phosphor dispersed the remaining in silicone resin.

As shown in Fig. 1 the size of the red QD is on the average 1/1000 of the YAG phosphor thus the chance of agglomeration and localization of the red QD becomes high in case of device pcWLED-1 which was made by direct mixing of the two phosphors. We then examined the optimum ratio of YAG phosphor to red QD in the pcWLEDs by using the separate mixing method of phosphors, i.e. the QD was mixed in silicone resin and then mixed again with the YAG/silicone mixture. The best combination of YAG and red QD phosphor was obtained at the ratio of YAG:QD = 5.0:0.5wt% as shown in Table 2 and Fig. 3 in which red QD peak was clearly observed.

The data in Table 3 and Fig. 4 exhibit the difference in the structure of phosphor encapsulation. The devices (pcWLED-3 to 5) in Table 2 were fabricated with the encapsulant in which the red QD/silicone and YAG/silicone were mixed together at same time whereas devices (pcWLED-6 to 8) in Table 3 were fabricated by layer-by-layer encapsulation, i.e. first YAG/silicone was dispensed on top of InGaN LED chip and heat cured to a tacky-free stage and then red QD/silicone was dispensed followed by full heat curing. As shown in Fig. 4 the device pcWLED-7 with optimum ratio of YAG phosphor to red QD exhibited

Table 3. Color coordinates, CRI (Ra) and efficiency (K) of pcWLED encapsulated with YAG phosphor and QD

Device No.	Coordinates (x, y)	Ra	K (lm/W)
pcWLED-6	(0.29, 0.30)	79	71
pcWLED-7	(0.31, 0.29)	82	87
pcWLED-8	(0.32, 0.27)	79	80

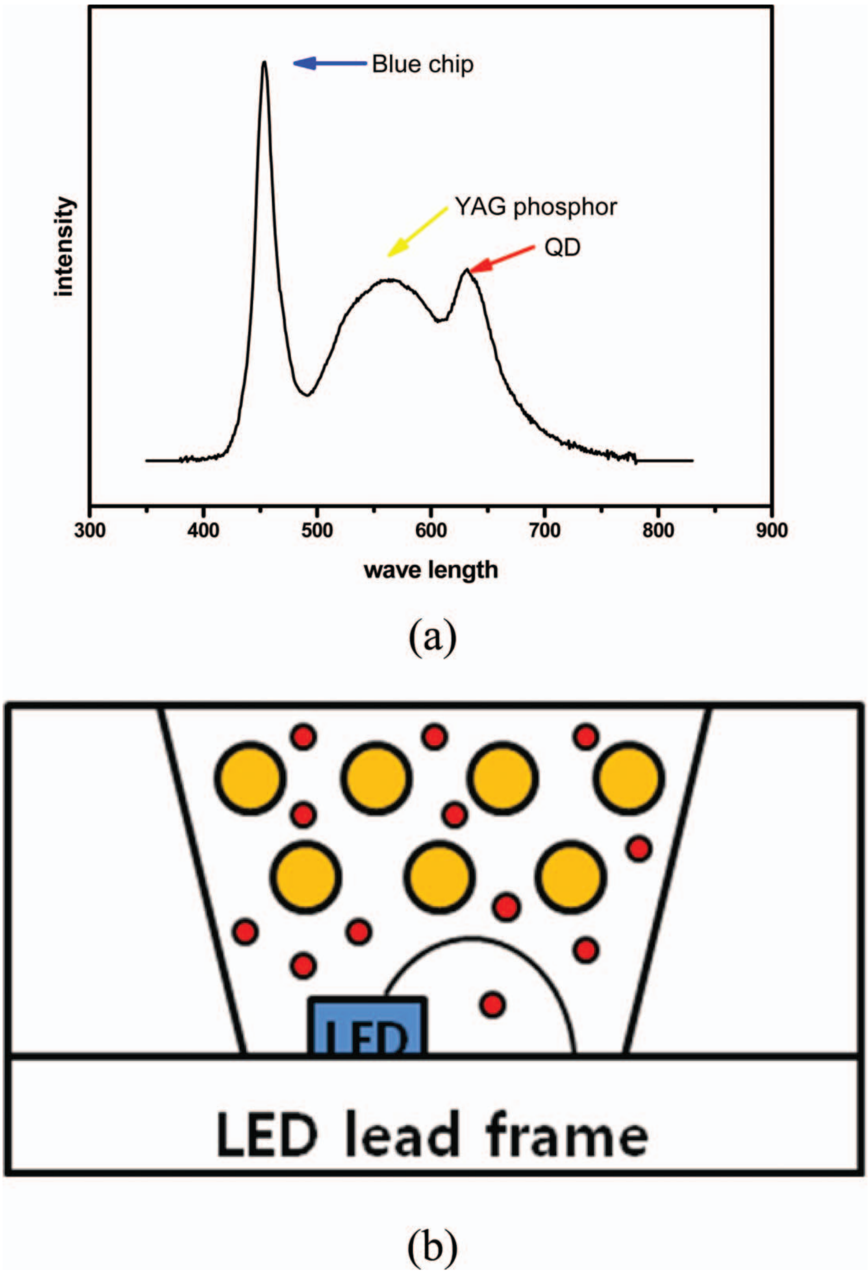

Figure 3. (a) The PL emission spectrum and (b) schematic diagram of the pcWLED encapsulated with YAG phosphor and red QD.

good color coordinates and improvement of efficiency and color rendering index in the same direction. These improvents seemed to be due to layer-by-layer encapsulation of YAG phosphor and red QD as shown schematically in Fig. 4(c) compared with the one shown in Fig. 3(b). As shown in Table 3 the layer by layer encapsulation of nano-size red QD could improve both the efficiency and CRI in the same direction. This improvement

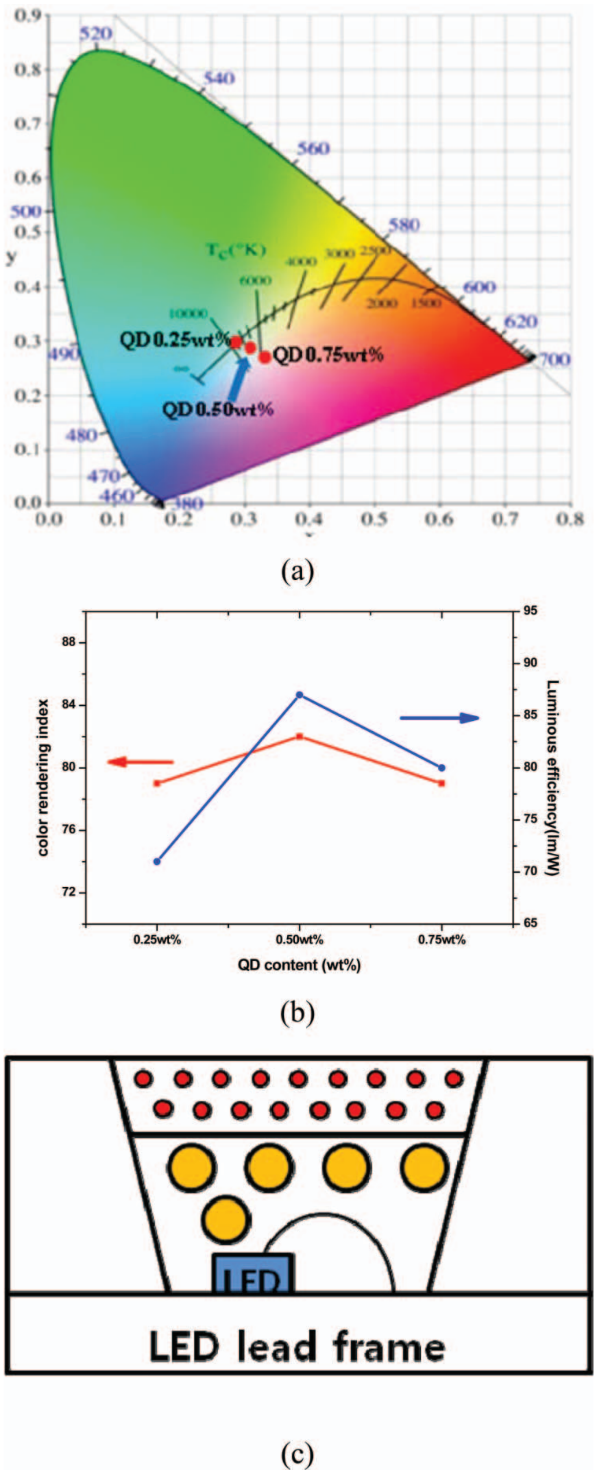

Figure 4. (a) Color corrdinates, (b) luminous efficiency/CRI, and (c) schematic diagram of pcWLED in which YAG phosphor and QD were encapsulated layer-by-layer method.

may by provided by the uniform distribution of red QDs and the efficient energy transfer of yellow (green) light from YAG phosphor to the thin layer of red QDs.

Conclusions

This study presents a new package structure for pcWLEDs that utilize layer-by-layer encapsulation of red-emitting CdSe QDs on top of the yttrium aluminium garnet (YAG) phosphor with silicone resin as encapsulating materials. The pcWLEDs made with YAG phosphor and QD encapsulated by layer-by-layer method exhibited that efficiency and color rendering index could be increased in the same direction while pcWLED made with same YAG and red QD together in one layer showed that efficiency and color rendering index exhibited trade-off property. This may be due to the large difference in sizes of YAG phosphor and red quantum dots (about 1/1000) which could easily lead to the agglomeration and localization of red QDs in the single layer encapsulation in which YAG phosphor and red QDs mixed together in the silicone resin matrix.

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