Efficient hybrid white light-emitting diodes by organic-inorganic materials at different CCT from 3000K to 9000K

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Abstract: The hybrid white light-emitting didoes (LED) with polyfluoren (PFO) polymer and quantum dot (QD) was investigated using dispensing method at the different correlated color temperature (CCT) for cool and warm color temperature. This result indicates that the hybrid white LED device has the higher luminous efficiency than the convention one, which could be attributed to the increased utilization rate of the UV light. Furthermore, the CIE 1931 coordinate of high quality white hybrid LED with different CCT range from 3000K to 9000K is demonstrated. Consequently, the angular-dependent CCT and the thermal issue of the hybrid white LED device were also analyzed in this study.

OCIS codes: (230.3670) Light-emitting diodes; (230.2090) Electro-optical devices.

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1. Introduction

Recently, white light emitting diodes (LEDs) has been widely used in solid-state lighting especially for the display and lighting application [1–3]. There are many advantages for white LEDs such as eco-friendliness, reliability and high efficiency to prevail over the traditional lighting sources [4]. Currently, the wavelength-converting white LEDs are the most common

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method to produce the white light, and the wavelength-converting agents include the phosphor, polymers and nanocrystals [5]. These agents can determine the overall luminous efficiency of the LEDs. Therefore, great efforts have been made to synthesize novel wavelength-converting materials in the recent years [6]. Specifically, the quantum dots (QD) has become the prominent materials due to their features of narrow bandwidths, broad absorption, and size-engineered band gap [7–10].

Nowadays, polymer light-emitting diodes (PLED) have attracted great interest due to the high emission efficiency and easy solution process [11–14], which are suitable to many specific lighting applications for interior design, cars and the display. Among the different polymer, polyfluoren (PFO) is the blue polymer that exhibit high photoluminescence (PL) efficiency and excellent chemical stability [15]. Therefore, several research labs have reported the use of the hybrid polymer/QD LEDs to obtain the excellent optical characteristic [16–19]. Park. *et al* proposed the white LED by using the polymer/quantum dot nanocomposite into blue-emitting poly(phenylene vinylene)-polyfluorene copolymers [18]. Huang. *et al* combined the PFO polymer with green and red QDs together to obtain the three-band white light [19]. Generally, the most common fabrication process for PLED is using the spin coating and only 5% of materials can stay on the chip, which increases the cost of the device [20]. As for other method, the dispensing method is addressed on the low cost and convenience, which is widely used in the industry [21]. Therefore, it is important to incorporate this method to reduce the waste and discuss about the device characteristic of PLED.

In this study, the hybrid white LED with the PFO materials and colloidal CdSe/ZnS QD are implemented in a UV LED by the dispense method, creating a simple device that generate the pure white color at the different correlated color temperature (CCT) for cool and warm color temperature. This hybrid structure has the higher luminous efficiency than the QD-based LED structure with the different injection current. In addition, the efficiency droop was significantly improved by the hybrid structure. Furthermore, the deviation angular-dependent CCT and thermal characteristic were also discussed for hybrid white LED.

2. Experiments

In this experiment, the hybrid white LEDs were fabricated using the dispensing method [22]. Figure 1(a) illustrates the schematic diagrams of the hybrid white LEDs device and Fig. 1(b) shows the sample of the hybrid LED device. The experimental flow was as follows: First, a 45 x 45 mil AlGaN/GaN ultraviolet HV-LEDs with an emission wavelength of 380 nm was bonded in the lead-frame package. Second, the PFO polymer and CdSe/ZnS QDs were uniformly blended with the PMMA and the mixture was dispensed in the package. For comparison, blue and yellow QDs were also uniformly mixed with the PMMA and designated as the conventional samples. The output power of the selected ultraviolet LED chips was 100 mW at a driving current of 120 mA. Moreover, to analyze the optical characteristic for the hybrid white LED, the white LED with different CCTs were fabricated by changing the portions of PFO and CdSe/ZnS QDs. The concentration ratio of the PFO polymer and CdSe/ZnS QDs is shown in Table 1.

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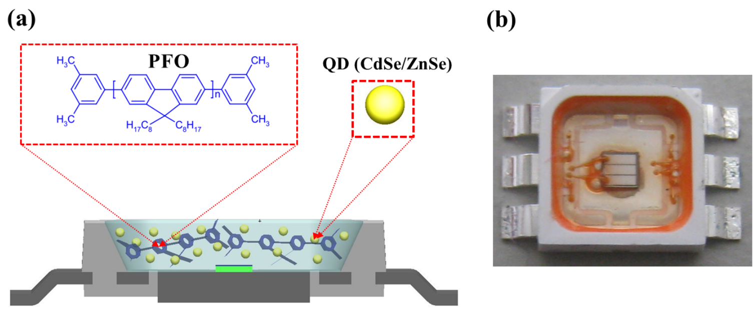

Fig. 1. (a) Schematic diagrams of hybrid LED device with the PFO materials phosphor structure (b) The picture of the hybrid LED device.

Table 1. The mixing volume ratio of RGB QDs for white LEDs with different color temperatures.

Ta(°C)	Red	Green	Blue
3000 K	1	2.5	0.5
5000 K	1	1.5	X
7000 K	1	1.5	X
9000 K	1	1	X

The absorption and PL spectra of PFO-toluene, blue and yellow QDs are shown in Fig. 2. The PL spectrum of PFO-toluene polymer shows over a wide spectrum from 405 nm to 520 nm in the visible region of and the strong emission peak is located at 442 nm. For the blue and yellow QD, the PL spectra centered at 460 nm and 560 nm for CdS and CdSe/ZnS QDs and the line width of PL for blue and yellow QDs was 20.5, and 35 nm, respectively. From the measured results, a UV pump source is preferred since the absorption for all luminaries is most strong in UV region. Thus, the UV LED with the wavelength 380 nm is used in this experiment to obtain the better conversion efficiency.

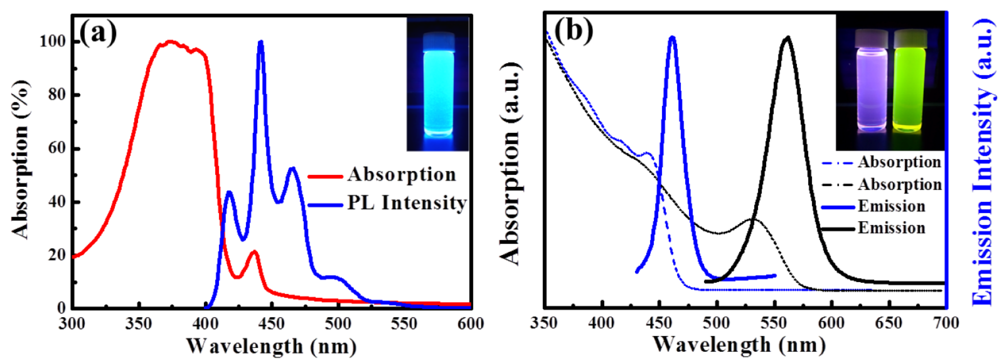

Fig. 2. The absorption and emission spectra of (a) PFO and (b) blue and yellow blue QD and the inset picture is the picture of PFO and blue and yellow blue QD.

Figure 3 shows the reflection and transmission of the hybrid LED device with PFO polymer and yellow QDs and the reference sample with wavelength from 300 to 800 nm. The reflection of the blue and yellow blue QD sample is slightly higher than the hybrid LED device especially in the visible region, resulting in lower light output. For the hybrid LED device with PFO polymer, the value of transmission is higher the reference in the range of 300-450 nm and yellow region because of higher conversion efficiency of PFO material and yellow QD, which has the benefit of the lumen efficiency enhancement. Furthermore, the trend of the transmission measurement has shown to have favorable agreement with the emission spectra in Fig. 4(a).

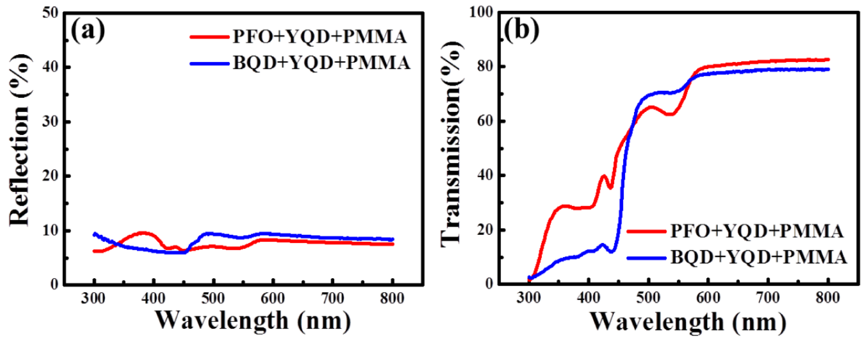

Fig. 3. (a)The reflection and (b) transmission of the hybrid LED device with PFO polymer and yellow QDs and the reference sample with wavelength from 300 to 800 nm.

3. Results and discussion

The emission spectra of hybrid LED device with PFO polymer and yellow QDs and the reference sample are shown in Fig. 4(a). These structures had the same CCT at approximately 5000 K, and both operated at a current of 120 mA. The white hybrid LED device produced the higher intensity in blue and yellow components. Moreover, the lumen flux and the luminous efficiency measured using a calibrated integrating sphere is plotted in Fig. 4(b) as a function of injection currents ranging from 20 to 150 mA. The luminous efficiency of hybrid LED device with PFO polymer and yellow QDs with UV LED source is about 13 lm/W and shows 1.8 times higher than the reference sample (7.2 lm/W) at the 20mA. This result indicated that the combination of PFO polymer and yellow QDs could be a potential competitor in the replacement of phosphors. It is true that the WLED has the higher luminous efficiency in the market (303 lm/Watt by Cree in 2014) [23], but the advantages of hybrid LED device with PFO polymer and yellow QDs resides in high CRI value and flexible device. In our study, the CRI of the hybrid LED device can easily achieve 85-90, which is better than traditional white LED. Moreover, compared to other studies related to quantum dot LED [24–26], the luminous efficiency of hybrid LED device is compatible and should be considered for the applications in the solid state lighting.

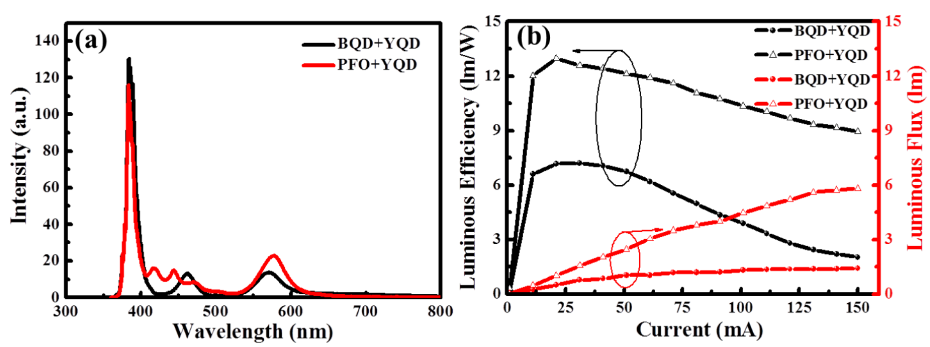

Fig. 4. (a) The emission spectra (b) Luminous flux and the luminous efficiency of hybrid LED device with PFO polymer and yellow QDs and the reference sample with 5000 K driven at the current from 20 to 150 mA.

Furthermore, the normalized external quantum efficacy (EQE) of the PFO polymer and blue QD with UV LED sample is shown in Fig. 5(a). The droop of EQE of the hybrid LED device and reference sample were 4.7% and 22.4%, respectively. Therefore, in this

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experiment, PFO polymer with UV LED can help to reduce the efficiency droop in the white LED. Figure 5(b) shows the PL quantum yield of the hybrid LED device with PFO polymer and yellow QDs and the reference sample with wavelength driven at the current from 20 to 150 mA. The PLQY of hybrid LED device with PFO polymer is about 17%, which is higher than the reference sample. One thing noted here in Fig. 5(b) is the universal reduction of quantum efficiency of the PFO and QD between the solution based and solid-phase based measurements, which can be attributed to the possible degradation during the solidifying process (such as self-assembly in QD) [7], and we are working on the improvement of this situation currently. Figure 6 shows CIE 1931 coordinate of the white hybrid LED with different CCT ranging from 3000K to 9000K. The coordinate of these samples are (0.40, 0.34), (0.35, 0.37), (0.31.0.29) and (0.29, 0.28), respectively. All the samples are located in the white region for CIE 1931 and the pure white color lighting source with different CCT were demonstrated in this study.

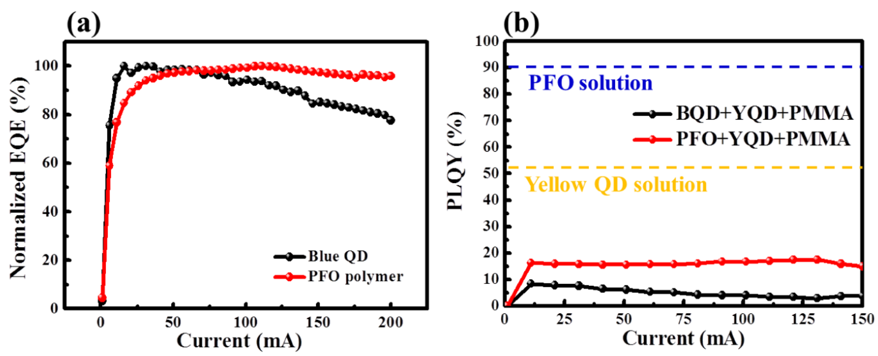

Fig. 5. (a). The normalized external quantum efficacy of the PFO polymer and blue QD with UV LED sample (b) PL quantum yield of the hybrid LED device with PFO polymer and yellow QDs and the reference sample with wavelength driven at the current from 20 to 150 mA.

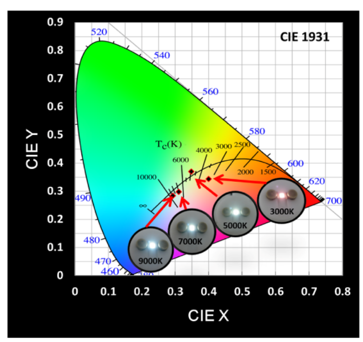

Fig. 6. CIE 1931 coordinate of the different correlated color temperature hybrid LED.

To understand the device optical characteristic, the angular-dependent CCT of the PFO with yellow QD at 5000K is analyzed as shown in Fig. 7(a). The uniformity of CCTs, which can be defined as the maximum CCT minus the minimum CCT, is treated as one of the important parameters of the light quality of the WLEDs [21]. The nonuniform CCTs between the normal and larger angles is called the yellow ring phenomenon which is not favorable to the specific application such as medical and building lighting. The CCT deviation of hybrid LED devices with PFO polymer and yellow QDs was 380 K in range of −70 to 70 degrees, which is better than the traditional dispensed phosphor structure [27]. This deviation can be further reduced by the installation of Distributed Bragg reflector (DBR) structure and nanoparticle scattering effect [27,28]. In addition, the normalized PL emission of hybrid LED device at various ambient temperatures from 20 to 70 °C is demonstrated, as shown in Fig. 7(b). With the increase of the temperature, the intensities of the PFO polymer and yellow QD are slightly reduced due to the thermal effect [29,30]. The thermal effect is still the crucial issue to emphasize the performance of LEDs. To keep the efficiency of the polymer devices, the remote type might be considered as the next step.

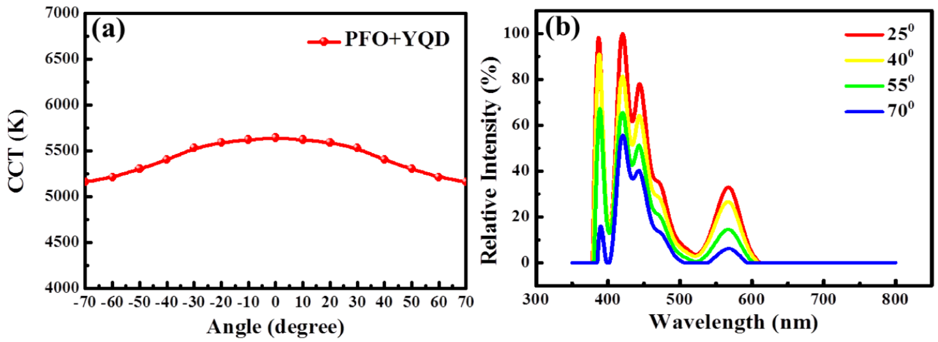

Fig. 7. (a) The angular-dependent correlated color temperature of the PFO with yellow QD with 5000K (b) The emission spectra of the PFO with yellow QD with the temperature from 25°C to 70°C.

4. Conclusion

In conclusion, the hybrid white LEDs were investigated—including AlGaN near UV-LEDs, PFO polymer, and CdSe/ZnS QDs. The results indicated that the higher luminous efficiency of the the hybrid white LEDs, compared with the conventional QD LED device. Moreover, the pure white color with different CCT for cool and warm color temperature is proposed in 1931 CIE coordinate. Furthermore, the CCT deviation was 380 K in range of −70 to 70 degrees for hybrid LED device.

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