Multi-color-emitting quantum dot-based white LEDs

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Research on white light-emitting diodes (LEDs) based on multi-color-emitting quantum dots (QDs) is carried out in this Letter. The equations of luminous efficiency (LE), color rendering index (CRI), chromaticity coordinates (x, y), and color temperature (T_c) of white LEDs are obtained, according to the spectral-LE function Φ of LED chips and QDs. The calculated results indicate that the values of the performance parameters of QD-based white LEDs are closely related and proportional to the QDs' fluorescence spectra, and white LEDs with a high LE and a high CRI may be fabricated based on QDs. We have provided theoretical guidance for preparing such white LEDs.

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White light-emitting diodes (LEDs) have consistently taken a significant market share in lighting and display applications owing to their excellent properties, such as high brightness, small volume, and long service life[1–4]. Current commercial white LEDs often consist of a blue-emitting InGaN-based chip and yellow $YAG{:}Ce^{3+}$ phosphors. Such white LEDs have a poor color rendering index (CRI) due to the lack of red components in the spectrum[5]. Researchers have proposed a new method of adding small amounts of nitride-based red phosphors and aluminate-based green phosphors to improve the CRI of white LEDs[6]. However, the drawbacks of high cost and self-absorption between different substrates prevent their wide usage in white LEDs.

In order to overcome the disadvantages of traditional phosphors, in recent years, many research teams have used semiconductor quantum dots (QDs). Semiconductor QDs, a kind of new luminescent material, are able to achieve a higher CRI due to their larger light absorption cross sections, higher color saturation, and tunable emission wavelength. In 2006, Song *et al.* reported a method of coating blue LEDs with green- and red-emitting CdSe/ZnSe QDs to improve the CRI of white LEDs to 91[7]. In 2012, Shen *et al.* prepared white LEDs by adding CdSe/CdS/ZnS QDs to nano-$YAG{:}Ce^{3+}$ phosphors, and the CRI was also 91[8].

Presently, many research groups have studied the performance parameters of QD-based white LEDs through related experiments[7–10]. White LED devices often need multi-color-emitting QDs because the performance parameters of single QD-based white LEDs are similar to $YAG{:}Ce^{3+}$-based white LEDs. However, a related theoretical analysis of multi-color-emitting QD-based white LEDs has not been reported, and no simple calculation formulas have been given. The theoretical calculation formulas of the performance parameters of two-color-emitting QD-based white LEDs are given in this Letter. Different from traditional phosphors, the fluorescence peak of QDs may be artificially adjusted, and the adjustment range covers the whole spectrum of visible light. The absorption cross section and quantum yield (QY) can be also directly measured by experiments. These advantages support the theoretical analysis of the performance parameters of QD-based white LEDs. The results obtained also provide guidance for the assessment of the performance parameters of white LEDs and their preparation.

Fluorescence peaks of LED chips (λ_{LED}) can be adjusted by the active layer composition ratio of chip substrate InGaN/GaN. Fluorescence peaks of QDs (λ_{QD}) depend on the QDs' size and impurity property. The emission spectra of LED chips $(P_{\mathrm{LED}}(\lambda))$ and QDs $(P_{\mathrm{QD}}(\lambda))$ present a symmetric Gaussian distribution, and the spectrum can be fitted with a Gaussian function according to the fluorescence peaks and the full width at half-maximum (FWHM)[11]. Therefore, the spectral luminous efficiency (LE) functions of LED chip (Φ_{LED}) and QDs (Φ_{QD}) are expressed as

$$\Phi_{\mathrm{LED}} = K_m \cdot \int P_{\mathrm{LED}}(\lambda) V(\lambda) \mathrm{d}\lambda, \tag{1a}$$

$$\Phi_{\mathrm{QD}} = K_m \cdot \int P_{\mathrm{QD}}(\lambda) V(\lambda) \mathrm{d}\lambda, \tag{1b}$$

where K_m is the biggest spectral-LE function of photopic-vision (according to the theoretical calculation value of international practical temperature scale IPTS–68, $K_m = 683$ lm/W), and $V(\lambda)$ is spectral-LE function of photopic vision.

The LE of white LEDs is decided by the ratio of luminous flux emitted by the light source to the electric power consumed. Hence, the LE of two-color-emitting QD-based white LEDs can be expressed as

$$L = \frac{\eta_{\mathrm{LED}}}{1-\beta_1-\beta_2+\frac{\lambda_{\mathrm{QD1}}}{\lambda_{\mathrm{LED}}}\cdot\frac{\beta_1}{\eta_{\mathrm{QD1}}}+\frac{\lambda_{\mathrm{QD2}}}{\lambda_{\mathrm{LED}}}\cdot\frac{\beta_2}{\eta_{\mathrm{QD2}}}} \times [(1-\beta_1-\beta_2)\cdot\Phi_{\mathrm{LED}}+\beta_1\cdot\Phi_{\mathrm{QD1}}+\beta_2\cdot\Phi_{\mathrm{QD2}}], \tag{2}$$

where η_{LED} is the electro-optical energy transfer efficiency of the LED chip, which can be obtained by the ratio of the LED chip's optical power to the electric power. η_{QD1} and η_{QD2} are the QYs obtained by the ultraviolet absorption spectrum and the fluorescence emission spectrum of the QDs. β_1 and β_2 are the proportionality constants of the QDs' fluorescence spectrum in the white light spectrum.

According to Eq. (2), the LE may be different with different fluorescence peaks of λ_{LED} or λ_{QD}. Obviously, if η_{LED} and η_{QD} are higher, the LE will be higher as well. If the LED chip and QDs are confirmed, the LE is closely related to β_1 and β_2. Common parameters of LED chip and QDs are chosen as: $\lambda_{\mathrm{LED}} = 455$ nm, FWHM = 25 nm, $\eta_{\mathrm{LED}} = 0.5$, $\lambda_{\mathrm{QD1}} = 535$ nm, FWHM = 55 nm, $\eta_{\mathrm{QD1}} = 0.8$, $\lambda_{\mathrm{QD2}} = 615$ nm, FWHM = 85 nm, and $\eta_{\mathrm{QD2}} = 0.8$. The relation of LE and β_1 (β_2) may be clearly described by a three-dimensional diagram, as shown in Fig. 1. Figure 1 shows that most of the LE values of QD-based white LEDs are larger than 100 lm/W. With the increase in the value of β_1, the LE value increases faster than β_2, indicating that the green-emitting QD has a major contribution to the LE value.

The value of the LE shown in Fig. 1 is based on chromaticity coordinates acquired by[11]:

$$X = \int X(\lambda)P(\lambda)\mathrm{d}\lambda, \tag{3a}$$

$$Y = \int Y(\lambda)P(\lambda)\mathrm{d}\lambda, \tag{3b}$$

$$Z = \int Z(\lambda)P(\lambda)\mathrm{d}\lambda, \tag{3c}$$

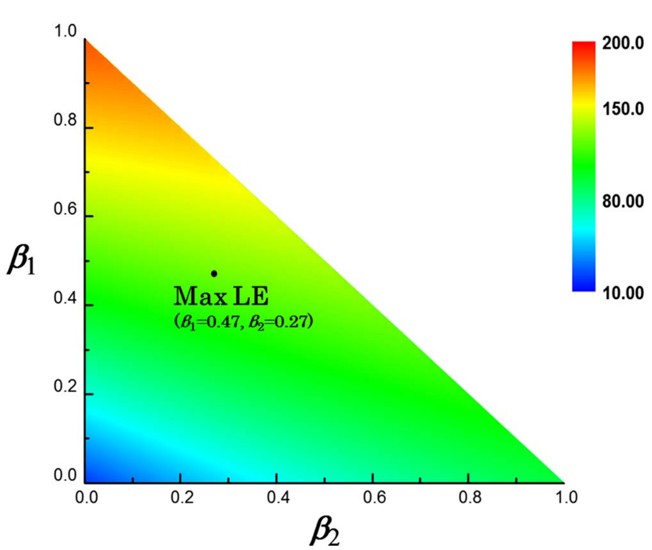

Fig. 1. Relation of LE and β_1 (β_2).

where $X(\lambda)$, $Y(\lambda)$, and $Z(\lambda)$ are tristimulus values stipulated by CIE. As the FWHM is smaller, the chromaticity coordinates of LED chip and QDs are closer to those of monochromatic light.

If we use N ($N > 2$) kinds of QDs, Eq. (2) may be changed to

$$L = \frac{\eta_{\mathrm{LED}}}{1-\sum_{i=1}^{i=N}\beta_i+\sum_{i=1}^{i=N}\frac{\lambda_{\mathrm{QD}i}}{\lambda_{\mathrm{LED}}}\cdot\frac{\beta_i}{\eta_{\mathrm{QD}i}}} \times \left[\left(1-\sum_{i=1}^{i=N}\beta_i\right)\cdot\Phi_{\mathrm{LED}}+\sum_{i=1}^{i=N}\beta_i\cdot\Phi_{\mathrm{QD}i}\right], \tag{4}$$

which can be applied to a single QD as well.

The CRI is another important performance parameter of white LEDs. The color emitted by a light source is determined by the emission spectrum, which is related and proportional to the different spectra under the conditions that the LED chip and QDs were chosen with certain values of the λ_{LED} and FWHM. That is, the CRI is closely related to β_1 and β_2, as shown in Fig. 2. We can see that β_1 and β_2 have great effect on the CRI value in Fig. 2. Figure 2 shows that most of the CRI values of multi-color-emitting QD-based white LEDs are larger than 70, and when the β_1 value is larger than β_2, most of the CRI values are less than 70, as shown in Fig. 2. From Fig. 2, we can see that with the increase in the value of β_2, the CRI value increases faster than β_1, indicating that red-emitting QDs have a major contribution to the CRI value.

The CRI value in this Letter is calculated with the "colorimetry method" by the CIE formulated in 1965 and revised in 1974[12,13], and it is given as follows:

$$Ra = \frac{1}{8}\sum_{i=1}^{i=8} R_i, \tag{5}$$

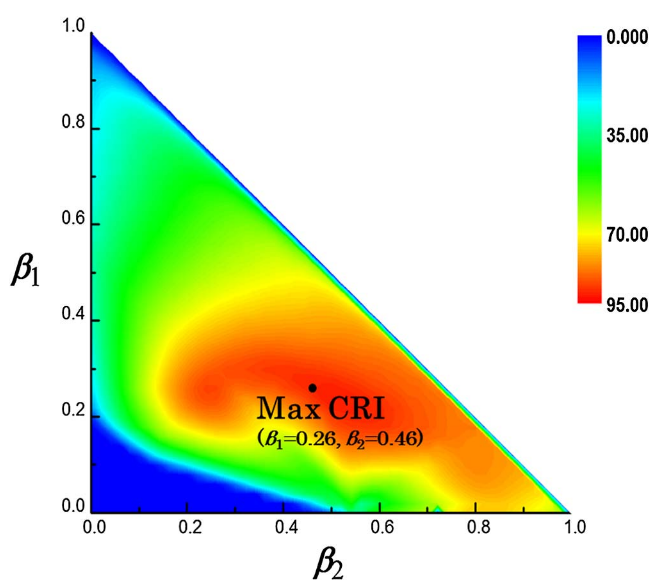

Fig. 2. Relation of CRI and β_1 (β_2).

where $R_i = 100 - 4.6\Delta E_i$ is a special CRI. ΔE_i is a chromatic aberration.

The corresponding β_1 and β_2 values of the maximum LE and the maximum CRI may be obtained from Figs. 1 and 2, and then the related CRI and LE values may be acquired according to the β_1 and β_2 values. The white light spectra are fitted as well, as shown in Fig. 3(a). Therefore, related chromaticity coordinates may be calculated by Eq. (3) and T_c will be obtained by[14]:

$$A = \frac{x - x_0}{y - y_0} = \frac{x - 0.329}{y - 0.187}, \tag{6a}$$

$$T_c = 669A^4 - 779A^3 + 3660A^2 - 7047A + 5652, \tag{6b}$$

where x and y are the chromaticity coordinates of the white LEDs, A is the reciprocal of the isotemperature line slope.

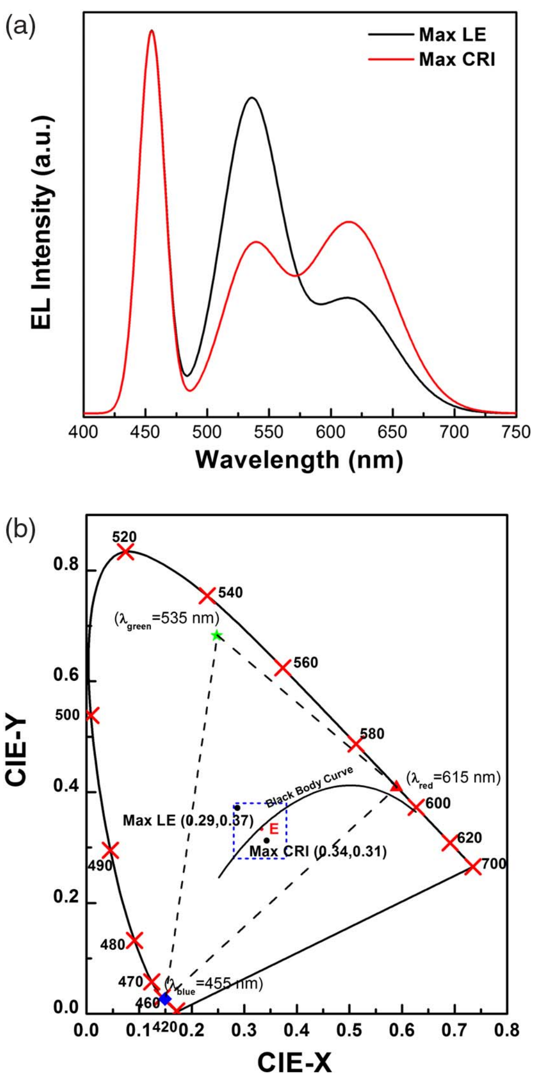

Fig. 3. (a) The white light spectra with the maximum LE and the maximum CRI, and (b) the CIE diagrams of white LEDs with the maximum LE and the maximum CRI. The square indicates the white light section[9].

According to the results of the calculations, the device obtained is of white light[9] with a maximum LE of 121 lm/W, a CRI of 68, an (x, y) value of (0.29, 0.37), and a T_c of 7371 K[5], where $\beta_1 = 0.47$ and $\beta_2 = 0.27$. In the experiment, the low LE results mainly from the serious self-absorption and inhomogeneous broadening of the QDs. In addition, the heat dissipation, reflectivity, and packaging structure of the device leads to low LE as well. Further, a device of white light with a maximum CRI of 92, an LE of 97 lm/W, an (x, y) value of (0.34, 0.31), and a T_c of 4956 K is superior to green and red phosphors-based white LEDs[6], where $\beta_1 = 0.26$ and $\beta_2 = 0.46$. It was reported that a green $SrSi_2O_2$:Eu- and red $CaSiN_2$:Ce-based white LED showed a high CRI of 90.5; however, the LE of the device is only about 30 lm/W[15]. Such a low LE may result from the serious self-absorption of the phosphors. Hence, the present green- and red-emitting QD-encapsulated white LEDs have sufficient LE compared to other reported white LEDs based on red and green phosphors. Figure 3(b) shows the CIE diagram of white LEDs with the maximum LE and maximum CRI, and the (x, y) values are close to (0.33, 0.33) and marked with E.

In the white light section, some points with CRI values exceeding 70 and LE values exceeding 80 lm/W are given, as shown in Fig. 4. From Fig. 4, we can see that most of the CRI values of white LEDs with LE values exceeding 100 lm/W are larger than 80, which indicates that a device based on green- and red-emitting QDs is helpful for improving the CRI of YAG:Ce^{3+}-based white LEDs with the same high LE[5]. Most of the LE values of white LEDs with CRI values exceeding 85 are larger than 95 lm/W, which indicates that a device based on green- and red-emitting QDs is also superior to white LEDs based on green and red phosphors[4,13].

When we prepare white LEDs, the white light spectrum is fitted first and the white LEDs are packaged according to the ratio of LED chips to QDs.

Based on multi-color-emitting QD-based white LEDs, the calculation formulas of LE, CRI, chromaticity

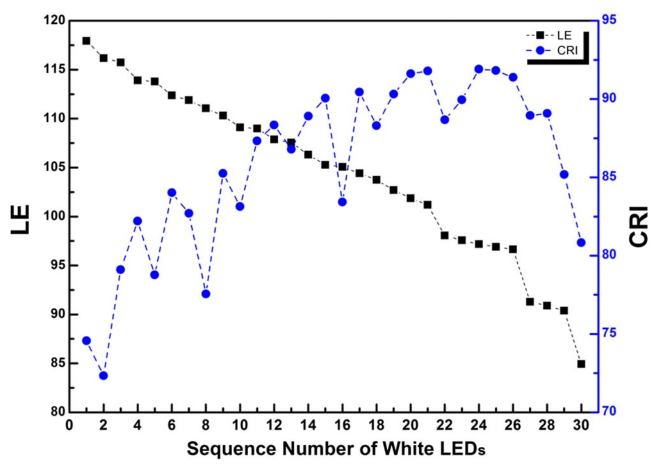

Fig. 4. Some points with CRI values exceeding 70 and LE values exceeding 80 lm/W in the white light section.

coordinates, and T_c of white LEDs are given according to the spectral-LE function (Φ) of LED chips and QDs. According to analysis of the calculation formulas, the performance parameter values of white LEDs are closely related and proportional to the QDs' fluorescence spectra. The performance parameters of white LEDs based on green- and red-emitting QDs are calculated, and a device of white light with a maximum LE of 121 lm/W is produced. Furthermore, a device of white light with a maximum CRI of 92 and an LE of 97 lm/W is superior to green and red phosphors-based white LEDs. It has been nice to see that most of the devices will be obtained with CRI values exceeding 80 and LE values exceeding 100 lm/W in the white light section. If we tune the peak wavelength or FWHM, the emission spectra and the spectral-LE functions will change. Then, the LE, CRI, chromaticity coordinates, and T_c values of white LEDs will change as well. White LEDs will be fabricated according to the ratio of LED chips to QDs obtained by the fitted white light spectrum. The formulas given are applicable to the theoretical calculations of the performance parameters of white LEDs with all known variables. Besides lighting, another important application of QDs is to use green and red QDs for display backlighting[16,17]. We have provided theoretical guidance for scientific research and practical production.

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