A high quality liquid-type quantum dot white light-emitting diode

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This study demonstrates a novel package design to store colloidal quantum dots in liquid format and integrate them with a standard LED. The high efficiency and high quality color performance at a neutral white correlated color temperature is demonstrated. The experimental results indicate that the liquid-type quantum dot white light-emitting diode (LQD WLED) is highly efficient and reliable. The luminous efficiency and color rendering index (CRI) of the LQD WLED can reach 271 lm W⁻¹ and 95, respectively. Moreover, a glass box is employed to prevent humidity and oxygen erosion. With this encapsulation design, our quantum dot box can survive over 1000 hours of storage time.

Introduction

Recently, colloidal quantum dots (QDs) have attracted industrial attention because of their unique properties such as high quantum yield, minimal backscattering, size dependent tunable bandgap, and narrow emission full width at half maximum.¹⁻⁷ As a novel technology in this field, QDs offer more variety in color mixing. In the past, high quantum efficiency and an excellent color-rendering index were achieved by multishell QDs and co-doping QDs in a phosphor.³,⁸ Core–shell structures have been employed to enhance the quantum yield of QDs and derive high photoluminescence efficiency.⁸,⁹ QDs can also be applied in some premium products such as displays with a high color gamut and WLEDs.¹⁰⁻¹⁴ As for the methods to dispense QDs, several groups have reported successful results in transfer printing,¹² pulsed spray,¹ inkjet printing¹¹ and mist coating.¹⁴ Furthermore, the 30 nm emission bandwidth of QDs can yield a higher degree of color purity compared with the estimated 100 nm bandwidth of monochromatic phosphor-converted LEDs.¹⁵,¹⁶

One major concern in these QD devices is the reduction in quantum efficiency when the solvent is dried up. When the QDs are dispersed in solvent, their light emission capability is much better than in the solid phase, due to the self-aggregation effect.¹⁷,¹⁸ Another issue accompanying solidification is the so-called “coffee ring” effect which results from the migration of solutes toward the edge of droplets during the drying process.¹⁹

In this study, a liquid-type QD white LED is demonstrated as an efficient color-conversion layer in UV LED packages. We use a glass material to protect the quantum dot material from drying. This method can increase quantum dot efficiency and reliability. The white liquid-type quantum dot LED is shown to have a high color rendering index (CRI) at a correlated color temperature (CCT) of 4360 K.

Experimental

In the sample preparation, two types of device were fabricated at the same time for comparison: one is a remote QD type (as our reference sample), and the other is a liquid type QD device. Fig. 1(a) shows the structure and process flow of the remote structure QD. We use PDMS to fill the 5070 type package. After the PDMS material was cured, an illuminating layer which contains QDs and PMMA was dispensed onto the LED package surface. To pump these QDs, a UV LED chip was installed in this 5070 package. The UV LED chips are first attached to a sub-mount. Then, the gold-wire bonding method was used to connect the anode and cathode pads. The chip size is 45 mil × 45 mil and the nominal power output of the UV chip (SemiLEDs EV-D45A) is 240 mW at 350 mA and the emission wavelength is 365 nm at a 350 mA driving current. Real device measurement yields a UV optical power (watts) to

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electrical power \((\text{watt})^{-1}\) ratio of 0.091 or 9.1%. Fig. 1(b) illustrates the process flow of the liquid-type QD white LED. The procedure is as follows: first, the glass substrate was cut into thin strips with a size of \(3.0 \text{ cm} \times 1.5 \text{ cm}\). Second, four of these thin strips were sandwiched in between two larger pieces of glass. Third, an appropriate gap was left such that the air can ventilate when the liquid QDs are injected. Finally, the gaps were sealed with an epoxy-based glue to finish the liquid QD process. The thickness of the glass slide is 0.1 cm and thus the overall volume which can accommodate the QD solution is \(1.5 \text{ cm} \times 3 \text{ cm} \times 0.1 \text{ cm} = 0.45 \text{ cm}^3 = 0.45 \text{ ml}\). Silicone is applied into the 5070 cup using a direct dispensing method. Under normal operation, the UV LED is based at 100 mA and the normal power is 43 mW. Considering the area of the 5070 package, which is 0.25 cm\(^2\), the pumping intensity is 172.8 mW cm\(^{-2}\). Both the remote quantum dot structure and liquid-type quantum dot structure were fabricated with the same quantum dots and characterized under the same conditions (i.e. the same UV chip initial brightness, and the same humidity and temperature).

As for QD characterization, we used a Horiba, FL-3 system to measure the spectrum and intensity. Fig. 2(a) and (b) show the UV-visible absorption and photoluminescence (PL) spectra of the five QD species used in this experiment. Our QDs were purchased from UT Dots, Inc. (web site: http://www.utdots.com). The QDs are dissolved in xylene and the different sized dots can provide different emission wavelengths. To have the emission wavelength of each QD sitting within ±10 nm of the specification, a certain level of control of the dot size distribution is necessary. The full width at half maximum (FWHM) of the emission spectrum is normally less than 35 nm for all products. The surface stabilizers of the dots are either octadecylamine (green and red) or oleic acid (blue and blue-green) and the concentration is 5 mg mL\(^{-1}\). The photoluminescence quantum yield (PLQY) of all QDs is higher than 50% according to the vendor’s datasheet. From the experimental results, the wavelengths of the blue, blue-green, green, orange, and red components were located at 450 nm, 490 nm, 535 nm, 590 nm and 630 nm, respectively. The FWHM of these emission spectra is approximately 20, 40, 40, 35, and 40 nm, respectively. Fig. 2(c) and (d) show the completed liquid type QD glass without and with UV pumping. The surrounding environment was totally dark when we took the picture shown in Fig. 2(d). So instead of white light, the strong scattering of the residual blue photons from the UV lamp (model number: UVGL-58) masked the weaker visible ones from the QDs and the whole film looked blue.

When the QDs with different colors were mixed, optimized procedures were carried out to obtain similar CCTs and the best CRI values. The quantity of each color of QD can determine the final color quality of the device. Microbalances were used to precisely measure the weight of each type of QD. The weight percentages for the reference and liquid QD samples are listed in Table 1.

### Measurement and analysis

Fig. 3(a) and (b) show the EL spectra of the remote QD type and liquid QD type devices under injection currents from 20 mA to 250 mA. The inset in Fig. 3(a) shows the current-dependent integrated intensity extracted from Fig. 3(a) and (b). All the measurements were performed in a calibrated integrated sphere. From the data, we see an overall improvement of 66.6% between liquid and remote samples at a 250 mA

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>450</th>
<th>490</th>
<th>535</th>
<th>590</th>
<th>630</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid QD</td>
<td>53.33%</td>
<td>13.34%</td>
<td>13.34%</td>
<td>13.34%</td>
<td>6.66%</td>
</tr>
<tr>
<td>Remote</td>
<td>57.70%</td>
<td>11.34%</td>
<td>11.34%</td>
<td>13.80%</td>
<td>5.82%</td>
</tr>
</tbody>
</table>
where 683 lm W is the eye sensitivity function, and $P$ is the QD LED. Because the QD layer is optically pumped with a driving current. After analyzing in more detail, the incremental percentages of the blue, blue-green, green, orange, and red color bands are 14.6%, 37.8%, 38.9%, 29.4%, and 39.4%, respectively at a 250 mA driving current.

The luminous efficacy of radiation (LER) is one of the indicators to show how efficient the emitter is in terms of white light generation. To calculate the LER, one can use the following expression:\(^\text{20}\)

$$\text{LER} = 683 \text{ lm W}^{-1} \frac{\int V(\lambda)P_{\text{white}}(\lambda)d\lambda}{\int P_{\text{white}}(\lambda)d\lambda}$$

where 683 lm W is a normalization factor, $V(\lambda)$ is the human eye sensitivity function, and $P_{\text{white}}(\lambda)$ is the spectral power density of the light source. In Fig. 4(a), the LER of the LED device with liquid-type quantum dots is approximately 271 lm W\(^{-1}\), and this value is higher than the 78 lm W\(^{-1}\) of the remote quantum dot structure. This improvement can be attributed to the high quantum yield of the liquid type device. In addition, Fig. 4(b) demonstrates the current-dependent CRI of different quantum dot structures. This characteristic is brought about by the five colors of the QDs in the spectra which can fulfill the CRI requirement.

To verify the claim that the liquid type device can preserve the quantum yield, one key factor to be tested is the PLQY of the QD LED. Because the QD layer is optically pumped with a UV source, the efficiency of converting the UV photons into visible ones can be expressed as\(^\text{21,22}\)

$$\text{PLQY} = \frac{\int_{\text{visible band}} \frac{\lambda}{hc} \times \left[ \rho_{\text{QD}}(\lambda) - \rho_{\text{ref}}(\lambda) \right] d\lambda}{\int_{\text{UV band}} \frac{\lambda}{hc} \times \left[ \rho_{\text{ex}}(\lambda) - \rho_{\text{ref}}(\lambda) \right] d\lambda}$$

where $\rho_{\text{ex}}$ and $\rho_{\text{ref}}$ are the integrated intensities of the UV excitation with and without the QD layer, and $\rho_{\text{QD}}$ and $\rho_{\text{ref}}$ are the spectral intensities of the visible band with and without the QD layer, respectively. By using the spectra of samples with and without the QD layer, we can estimate the PLQY values for both types of device. The PLQY of the liquid QD device is 33.87% and the reference remote QD sample is 31.32%. The number for the liquid QD case can be re-adjusted to 34% if the UV absorption of the glass slides, which is about 10% usually, is taken into account. A higher PLQY value of the liquid type device also justifies our initial idea of keeping QDs from solidifying.

Fig. 5(a)–(c) show the thermal images of the surfaces of regular LED, remote quantum dot and liquid-type quantum dot samples. Fig. 5(d) shows the current dependent surface temperatures among these three different types of device. The surface temperature can reach 200 °C at 250 mA in the remote case. This will reduce the efficiency of the quantum dots and cause a reliability problem.\(^\text{23}\) On the other hand, the liquid type QD LED can keep the surface temperature as low as 50 °C, which is advantageous towards both performance and reliability. As for the temporal behavior of the sample under UV excitation, surface thermal image measurements for a similar setup which contains QDs wrapped in a silicone like material with a UV LED packaged together were performed. The stabilization of the surface temperatures both under high
and low current injection is within 5 minutes based on the 30-minute observation.

To investigate the huge difference in the surface temperatures, we must understand more of the thermal transport characteristics of the package materials. The thermal conductivity of the glass is 1.05 W (m K)^{-1} and PMMA is 0.167–0.25 W (m K)^{-1}. Apparently the glass container of the liquid type device is a much better material for heat dissipation and the glass slides also possess a much larger area. Invoking Fourier’s law of heat conduction, we could obtain the thermal resistance (R) calculated as:

\[
\text{heat-transfer-rate} = \frac{\Delta T}{R}, \quad R \propto \frac{L}{\kappa A}
\]

where \(\Delta T\) is the temperature difference between two endpoints and \(R\) is the thermal resistance. In this simplified model, we could observe the significant difference made by the thermal conductivity and area of the device. From the calculation of the effective emission area, the heat dissipation capacity between remote QDs and liquid QDs is very different. The effective area of the liquid QD sample is 1.34 cm^2 and for the other device it is only 0.25 cm^2. On combining with a different material, a much larger thermal resistance (33.7 times under one-dimensional analysis) in the remote QD case is expected. This is the major cause of the much higher surface temperature detected. High levels of heat trapped inside the package can certainly reduce the efficiency of the QDs, while the liquid QDs will have a larger footprint and take up more space for setup.

Fig. 6(a) and (b) show the white light images of the remote quantum dot structure and liquid-type quantum dot structure under UV LED excitation. The pictures of Fig. 6(a) and (b) were taken using a generic digital camera (HTC® One®) and imported into Matlab® to extract the two-dimensional intensity profile shown in Fig. 6(c). By appropriately choosing the ratio between different QDs, both devices can achieve a similar CCT (4500 K) and high CRI (>90). The effective emission areas for the liquid QD and reference QD samples are quite different. From the 2D intensity profile as shown in Fig. 6(c), the emission area of the liquid QD device can be estimated as 1.34 cm^2, which is about five times that of the reference. But at the same time, due to the controlled output power of UV LEDs, the excitation source is kept the same and thus the comparison between the two types of samples should solely depend on the emission efficiency of the quantum dots. A larger emission area is helpful for thermal dissipation (as can be observed in Fig. 5) and further maintaining the quantum yield of the QD solution in our case, which eventually contributes to a better LER. The uniformity of the light intensity, if defined by the 10% variation of the maximum, can be as high as 91.2% of the emission area. Meanwhile, the luminous efficiency of the liquid QD device is about 7 lumens watt (electrical power)^{-1}.

After the initial characterization of the devices, the next important task is to test the longevity of this liquid QD LED. In the past, many results have shown serious degradation of the QD performance when the device is exposed to air.\(^7\)\(^17\)\(^25\) In our design, the glass container was sealed to prevent the solvent from drying and also to keep oxygen and water from reacting with the QDs. We hope this can help to preserve the quantum yield of the QDs over a long period of time. Fig. 7(a) and (b) show the emission spectra of the remote QD structure and liquid-type QD structure taken at various times when both devices are stored at room temperature. The measurement conditions for both devices is a 350 mA driving current and the measurements were tested at 0, 0.15, 0.3, 0.4, 0.5, 1, 20, 40, 72, 350, 500 and 1000 hours. The experimental results demonstrate that the liquid-type quantum dot structure has a stable and sustainable performance over a long period of time, as shown in Fig. 7(c). The efficiency reductions of the remote quantum dot structure and liquid-type quantum dot structure are 75% and 5% after 1000 hours of storage, respectively. The color rendering index shifts of the remote quantum dot structure and liquid-type quantum dot structure at a 350 mA current from 0 to 1000 hours are shown in Fig. 7(d). It is found that the color rendering indices of both structures quickly become stable after 0.5 hours. From these results, the liquid type of package not only maintains its intensity but also its color quality over a long storage time.

One concern about a possible change in the QD size distribution arises when the QDs are stored in the liquid phase. Under the current test conditions, which do not constantly shine the QD samples with UV photons, the interference from UV heating could be minimized. On the other hand, the self-
aggregation of QDs in the liquid phase over a long storage time should be discussed. To evaluate this without performing TEM, the emission spectrum of the QD layer holds the key. The emission spectrum of a QD ensemble usually represents the size distribution of this ensemble, because the size of a nanoparticle can determine the emission peak wavelength and the population of the same sized particle is proportional to the emission intensity. So the direct comparison between the peak positions and FWHM of the emission spectra can help us to understand the size distribution of the dots and thus the degree of aggregation. Fig. 7(b) provides a great opportunity for evaluating each QD’s variation during this long storage time. By using appropriate curve fitting, the position and FWHM of each peak can be found and the results are summarized in Table 2.

From this table, we could observe very little change between the 0th and 1000th hour of testing among the five different QDs we put into the glass slide. Certainly the nature of this storage test minimized the extreme thermal and UV illumination issues for the sample, but the constant performance and minimum aggregation that can be implied from this table demonstrate a potential solution for the long-term stability in this QD type device.

Table 2 The comparison of the linewidths and peaks among different QDs and elapsed time

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Elapsed time</th>
<th>QD1</th>
<th>QD2</th>
<th>QD3</th>
<th>QD4</th>
<th>QD5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linewidth (nm)</td>
<td>0th hour</td>
<td>22.67</td>
<td>45.94</td>
<td>44.67</td>
<td>26.84</td>
<td>24.35</td>
</tr>
<tr>
<td></td>
<td>1000th hour</td>
<td>23.51</td>
<td>46.99</td>
<td>43.88</td>
<td>26.84</td>
<td>25.21</td>
</tr>
<tr>
<td>Peak (nm)</td>
<td>0th hour</td>
<td>451.93</td>
<td>484.72</td>
<td>541.27</td>
<td>585.10</td>
<td>627.21</td>
</tr>
<tr>
<td></td>
<td>1000th hour</td>
<td>451.46</td>
<td>485.36</td>
<td>542.25</td>
<td>585.13</td>
<td>627.40</td>
</tr>
</tbody>
</table>

For the quantum dot white LED, the color deviation with different structures is used to evaluate the color stability for high-quality lighting applications. Therefore, the chromaticity coordinate shifts of the remote quantum dot and liquid-type quantum dot structures are recorded and shown in Fig. 8(a) and (b). As the time passed by, the chromaticity coordinates for the liquid-type quantum dot structure were stable. Moreover, the color deviation of a lighting system, \( \Delta u'v' \) is calculated as follows:

\[
\Delta u'v' = \sqrt{\left(\Delta u'\right)^2 + \left(\Delta v'\right)^2}
\]

where \( u' \) and \( v' \) are the chromaticity coordinates in the CIE 1976 diagram, and \( x \) and \( y \) are the chromaticity coordinates in the CIE 1931 diagram. The \( \Delta u'v' \) value indicates color shifts which might alter the CCT eventually. From the experimental results, the remote QD sample showed a moderate CIE coordinate-shift while the liquid QD sample remained almost the same after 1000 hours of storage. This clearly demonstrates the superiority of our design in terms of light quality which should be crucial for use as a next generation light source.

Conclusion

This study demonstrates a hybrid white LED with a liquid-type quantum dot structure to produce a stable and high color ren-
ndering index light source. We use a glass-slide-formed cavity to protect the quantum dots from environmental influences. The liquid-type quantum dot structure can maintain the quantum dot efficiency and reduce the thermal effect. This design can modify the emission spectrum easily and enhance the quantum yield of the QDs. The finished WLED, when pumped with UV light, can achieve a LER of 271 lm Wop⁻¹ with a 5% decrease after 1000 hours of storage. We believe that the liquid-type quantum dot WLED with high luminous efficiency is suitable for various high quality lighting applications in the near future.

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Notes and references

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