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# Applying InP/ZnS Green-Emitting Quantum Dots and InP/ZnSe/ZnS Red-Emitting Quantum Dots to Prepare WLED With Enhanced Photoluminescence Performances

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**ABSTRACT** Based on blue LED chips to excite Ce-doped yttrium aluminum garnet (YAG: Ce<sup>3+</sup>) yellow phosphors, InP/ZnS green-emitting quantum dots (QDs) and InP/ZnSe/ZnS red-emitting QDs are used as light conversion materials for WLEDs to improve the color rendering index (CRI) of the device and improve its color coordinates. We have proven this in previous work. But in the previous work, we only studied the CRI of the driving current from 5 mA to 100 mA. The CRI and the Commission International de L'Eclairage (CIE) chromaticity coordinates of the WLED device prepared before is not ideal under high current conditions. The emission peak position of InP/ZnSe/ZnS red-emitting QDs we used in previous work is 605nm. In this article, we adjusted the emission peak position of InP/ZnSe/ZnS red-emitting QDs to 611nm, and prepared WLED in the same way, which improved the problem that the CRI of WLED devices decreases rapidly and the chromaticity coordinates change greatly under high current conditions. The CRI of prepared WLED device in this article was increased to 91.0, the CIE chromaticity coordinates is (0.3365, 0.3334), and the correlated color temperature (CCT) is 5313 K. We also tested the dependence of the electroluminescence (EL) spectrum, CRI, CCT and chromaticity coordinates of the prepared WLED device on the current. Compared with the prepared WLED device before, the CRI of the WLED device prepared in this article has always remained above 90, hovering between 90  $\sim$  91, very stable. The chromaticity coordinate distribution is also very concentrated, the amplitude of the offset black body radiation is small, and it shows excellent color rendering and stable working performance. A 30-day aging test was performed on the prepared WLED device.

**INDEX TERMS** WLED, InP/ZnS QDs, InP/ZnSe/ZnS QDs, photoluminescence.

#### **I. INTRODUCTION**

Light emitting diode (LED) is a solid-state semiconductor device that is widely used in many areas of daily life such as life lighting, traffic directions, display backlights, and so on [1]. The white light spectrum produced by the commonly used blue InGaN LED chip to excite the yttrium aluminum garnet yellow phosphor (YAG:  $Ce^{3+}$ ), due to the lack of

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the red spectrum component, usually has a color rendering index (CRI) of less than 80 and does not have a good Commission International de L'Eclairage (CIE) chromaticity coordinate. Although we can now improve the CRI of WLED devices through the adjustment of green, yellow and red phosphors, the granularity of phosphors such as YAG is too large to meet the trend of the LED industry toward micro LEDs. The use of phosphors such as YAG should be minimized in the experiment. Studies have found that semiconductor quantum dots (QDs) have the advantages of high fluorescence

spectrum quantum yield (QY), wide absorption spectrum, adjustable size emission, high photo-oxidation resistance, low scattering effect, and good color saturation [2]. They are widely used in LEDs, solar cells, lasers, detectors, and biomarkers [1]. Therefore, it is proposed that the quantum dot material instead of the phosphor to generate white light is an effective solution.

In 2008, Wang *et al.* used blue InGaN chips to excite three different sizes of CdSe/ZnS QDs to make white LEDs, with a maximum CRI of 76 [3]. In 2009, Changyu Shen *et al.* used blue LEDs in combination with CdS/ZnS QD and YAG: Ce phosphors emitting red-orange light to increase the CRI value of mixed white LEDs to 86 [4]. In 2010, Chung, Shu-Ru and others used thermal deposition to synthesize core/shell CdSe-ZnS QDs with a peak/emission wavelength of 618 nm. The CRI value of a white LED that combines a blue LED with a 1: 1 weight ratio of phosphor and QD is increased by 90 [5]. In 2011, S Chandramohan *et al.* used core-type CdSe and core/shell-type CdSe/ZnS NC integrated on InGaN/GaN LEDs to prepare hybrid white light-emitting diodes with CIE chromaticity coordinates (0.356, 0.330) and CRI of 87.4 [6]. In the same year, XB Wang *et al.* synthesized CdSe/CdS/ZnS core/multi-shell QDs, combined green, yellow, and red emitting QDs and epoxy composite materials with blue InGaN LEDs to manufacture WLEDs. Its color coordinates are (0.35, 0.37) and CRI is 88 [2]. In 2015, Peng *et al.* produced warm white LEDs based on CdSe/ZnS colloidal QDs with  $CCT = 3778K$ , CIE color coordinates (0.36, 0.28) and CRI = 80.8 [7]. However, Cd is a heavy metal element and does not meet the requirements of non-toxic green and environmental protection. It is not environmentally friendly in the field of lighting, so it is necessary to find non-toxic and environmentally friendly QDs that replace Cd [8], [9]. In 2014, Chuang and Po-Hsiang *et al.* used CIS/ZnS QDs as a color converter, combining green emitting  $Ba<sub>2</sub>SiO<sub>4</sub>$ : Eu  $2^+$  phosphors and blue light emitting diodes, a highly efficient white light emitting diode with a high color rendering index of 90 was manufactured [10].

In 2015, X. T. Feng *et al.* used CQD as a single white light converter and used UV-LED chips as excitation light sources. The prepared WLED shows the corresponding color temperature (CCT) is 5227 K, and the color coordinate is (0.34, 0.38) [11]. In 2016, Park, Joong Pill, *et al.* used InP-based QDs and combined a very small amount of Mg cations as surface stabilizers to prepare WLED devices with Ra of 84.4 and CCT of 3799 K [12]. In 2017, ChihChun Hsiao and others mixed the green-emitting  $Lu_3Al_5O_{12}$ : Ce<sup>3+</sup> (LuAG) phosphor with CIS/ZnS QDs-resin, and dropped the QDs-phosphorus-resin mixture on top of the blue LED chip (InGaN) with 400 W ultraviolet light cures the device to form a WLED. The CRI, CCT and CIE chromaticity coordinates are 89, 5661K and (0.33, 0.29), respectively [13]. In the same year, Feng Li *et al.* prepared white LEDs (WLED) based on Cd0.1Zn0.9S/ZnS and Cd0.1Zn0.9S/ZnSe QDs. It has been concluded that the four-peak quantum dot light-emitting

diode (QLED) is superior to the two-peak quantum dot in terms of luminescence and visual characteristics [14].

In 2019, Dongyu Li and others used TBS-PBO as the electron blocking layer to manufacture blue QLED, which improved the charge transfer balance of the device. The device showed a significant brightness of 4635cd/m2, and the maximum EQE was 17.4%, much higher than the most advanced blue QLED. Provides a potential method for achieving high-brightness blue QLEDs [15]. In the same year, Ting Yuan *et al.* manufactured WLEDs by integrating W-CNQD phosphors into UV-LED chips, which have white light characteristics with CIE chromaticity coordinate and CRI of (0.35, 0.39) and 85, respectively [16].

In this article, based on the previously mentioned blue LED chip excited YAG:  $Ce^{3+}$  yellow phosphor, superimposed InP/ZnS green-emitting quantum dots (QDs) and InP/ZnSe/ZnS red-emitting QDs. On the basis of WLED made of light conversion material, by adjusting the emission peak position of InP/ZnSe/ZnS red-emitting QDs, a WLED device was prepared in the same way, which improved its CRI decreases rapidly under high current conditions, and the problem of large color coordinate changes, at the same time, the CRI of the prepared WLED device was increased to 91.0, the CIE chromaticity coordinate was (0.3365, 0.3334), and the CCT was 5313 K. Compared with other articles, the first advantage is the use of environmentally friendly and non-toxic cadmium-free quantum dots, and the second advantage is the high CRI. By comparing the EL spectrum, CRI, and CCT with a driving current of 5 mA  $\sim$  350 mA, the improved WLED device shows high-quality color rendering performance and very stable working performance.

#### **II. EXPERIMENT**

# A. MATERIALS AND EQUIPMENT USED IN THE **EXPERIMENT**

In the experiment, blue LED chips for packaging, YAG:  $Ce<sup>3+</sup>$ , silicone (6550A and 6550B), and UV glue (U-613) were purchased from the market. A field emission transmission electron microscope (JEM-2100F) was used to measure the size and morphology of the QDs. A fluorescence spectrophotometer (HITACHI 4500) and a UV-vis spectrophotometer (U-3900H) were used to measure the absorption characteristics and photoluminescence (PL) characteristics of QDs, respectively. The electroluminescence (EL) performance of the device was measured by an integrating sphere test system (HAAS-2000). Use the constant temperature and humidity box (GPS-3) for the aging test of the device.

# B. SYNTHESIS OF QDs

# 1) SYNTHESIS OF InP/ZnS GREEN-EMITTING QDs

Reagents for the synthesis of InP/ZnS green-emitting quantum dots include: zinc (II) chloride ( $\geq$ 98%), tris (diethylamino) phosphine (97%), indium (III) chloride (99.999%). Zinc stearate (industrial grade, 65%) was purchased from

Sigma-Aldrich and Olelamine (80  $\sim$  90%) was purchased from Acros Organics. Octadecene (90% technical content) was purchased from Alfa Aesar, and sulfur powder was purchased from Strem Chemicals.

Reference synthesis scheme based on indium halide and aminophosphine precursors: First, 160 mg (0.45 mmol) of indium (III) bromide and 300 mg (2.2 mmol) of chlorinated chloride were firstly used in 5.0 mL (15 mmol) of industrial oleylamine. Zinc (II) was mixed. The mixture was stirred and degassed at 120  $\degree$ C for 1 hour, and when heated to 180 ◦C under an inert atmosphere, 0.45 mL (1.6 mmol) of tris (diethylamino) phosphine (phosphorus: indium) Ratio = 3.6: 1) quickly inject into the above mixture. At 20 minutes, 1mL of saturated TOP-S (2.2 M) was injected. The temperature rose to 200 ◦C at 60 minutes. At 120 minutes, 1g of  $Zn$ (stearate)<sub>2</sub> was injected into 4mL of octadecene (ODE). The temperature rose to 220 ◦C. After 150 minutes, 0.7 mL of stoichiometric TOP-S (2.2 M) was injected and the temperature rose to 240 °C. At 180 minutes, 0.5 g of Zn(stearate)<sub>2</sub> was slowly poured into 2 mL of ODE. The temperature rose to 260 ◦C. At 210 minutes, the reaction was complete and the temperature was cooled. The InP/ZnS nanocrystals were then precipitated in ethanol and suspended in chloroform. The emission line width (fwhm) of InP/ZnS green-emitting QDs is 46 nm-63 nm, and PLQY is 60% [17], [18].

# 2) SYNTHESIS OF InP/ZnSe/ZnS RED-EMITTING QDs

The InP/ZnSe/ZnS QDs were synthesized by a previously reported potentially effective method, with an emission peak of 611nm, which was 5nm red-shifted compared to previous work. PLQY shows up to 73% and narrow emission line width (up to 40 nm). In the field of photoluminescence, organic long-chain ligands have little effect on photoluminescence efficiency, and the oleic acid ligands used in our word are generally 0.8nm long, and our InP core-shell quantum dots have 9.3nm. The effect of the spacing between the devices on the light emission is negligible. Long-chain ligands improve the stability of QD and will not cause QY to decrease [18], [19].

# C. PRODUCTION OF WLED

Similar to the method mentioned in the previous work, the packaging of white LEDs is divided into three layers, and a blue light chip with a peak wavelength of 450 nm is used for excitation. The blue LED chip generates blue light with a peak of about 450 nm under electrical excitation, and the yellow phosphor coated on the upper part of the LED chip is excited by part of the blue light to produce yellow light with a peak of about 570 nm. Mixed with the blue light transmitted through the phosphor to generate white light; the light formed after combining with InP/ZnS green-emitting QDs lacks the red factor, and the CRI value of the device is low; Finally, the InP/ZnSe/ZnS red-emitting QDs are coated on InP/ZnS green-emitting QDs surface, thereby generating white light, by controlling the concentration and amount of quantum dots to prepare WLED devices with excellent color coordinates and high CRI.

The specific preparation steps are as follows: first layer: Weigh 0.5 g 6550A, 0.5 g 6550B and 0.2 g YAG:  $Ce^{3+}$  for mixing, stir using a blender until the mixture is uniform, and the bubbles therein are removed. The obtained YAG:  $Ce^{3+}$ colloid was applied to the LED device in a spot coating manner, and cured in an oven at 150 °C for 5 minutes. Second layer: Centrifugally stir 500  $\mu$ l of InP/ZnS green-emitting QDs solution with a concentration of 70 mg/ml and 2 g of UV gel to mix well to form a QDs colloid. Add a small amount of InP/ZnS green-emitting QDs colloid to the cured yellow phosphor in the spot coating method, and then irradiate it under the ultraviolet lamp for curing. The third layer:  $400 \mu l$ of InP/ZnSe/ZnS red-emitting QDs (the emission peak is 606 nm) solution having a concentration of 30 mg/ml and 2 g of UV glue were centrifugally stirred until uniformly mixed to form an InP/ZnSe/ZnS red-emitting QDs colloid. An appropriate amount of InP/ZnSe/ZnS red-emitting QDs colloid was applied over the InP/ZnS green-emitting QDs colloid by spot coating and cured by irradiation under an ultraviolet lamp. This completes the packaging of the WLED I.

The method of preparing WLED II is similar to that of WLED I but the 400  $\mu$ l of InP/ZnSe/ZnS red-emitting QDs (the emission peak is 606 nm) solution is replaced by InP/ZnSe/ZnS red-emitting QDs solution with a peak wavelength of 611 nm.

# **III. RESULTS AND DISCUSSION**

A. MORPHOLOGY AND SIZE CHARACTERIZATION OF QDs Figure 1 (a) shows a picture of InP/ZnS green-emitting QDs under a transmission electron microscope (TEM). It can be seen that QDs are multi-layered plate-like particle structures with uniform dispersion. Randomly selected 100 QDs for size measurement. The particle size distribution of InP/ZnS green-emitting QDs is shown in figure 1 (b). It can be seen



**FIGURE 1.** (a) TEM image of InP/ZnS green-emitting QDs, inset is HRTEM image (b) Size distribution of InP/ZnS green-emitting QDs (c) TEM image of InP/ZnSe/ZnS red-emitting QDs, inset is HRTEM image (d) Size distribution of InP/ZnSe/ZnS red-emitting QDs.

that the particle size distribution of InP/ZnS green-emitting QDs is between 4.1 nm to 8.2 nm. The average size is 5.54nm. The inset of figure 1 (a) is a high-resolution transmission electron microscope (HRTEM) image of InP/ZnS green-emitting QDs, after measurement, the interplanar spacing of lattice fringes of InP/ZnS green-emitting QDs was 0.380 nm. The lattice structure of the QDs can be clearly seen.

Figure 1 (c) shows a TEM picture of InP/ZnSe/ZnS red-emitting QDs. It can be seen that the InP/ZnSe/ZnS red-emitting QDs are multi-layered plate-like particle structures. Randomly selected 100 QDs for size measurement. The particle size distribution of InP/ZnSe/ZnS red-emitting QDs is shown in figure 1 (d). It can be seen that the particle size distribution of InP/ZnSe/ZnS red-emitting QDs ranges from 7.13 nm to 14.22 nm. The average size was 9.30 nm. The inset of figure 1 (c) is a HRTEM picture of InP/ZnSe/ZnS red-emitting QDs, after measurement, the interplanar spacing of lattice fringes of InP/ZnSe/ZnS red-emitting QDs was 0.335 nm. Figure 2 is the X-ray diffraction (XRD) pattern of InP/ZnSe/ZnS red-emitting QDs. It can be seen that the XRD of the InP core before the ZnS shell is the phase of InP, and the XRD after the ZnS shell is only the ZnS phase, ZnS is coated on InP. It is proved that In/ZnSe/ZnS red-emitting QDs are core-shell structures.



**FIGURE 2.** XRD Characterization of InP/ZnSe/ZnS red-emitting QDs.

# B. PHOTOLUMINESCENCE PROPERTIES OF QDs

We used fluorescence spectrometer and UV-vis spectrophotometer to test the PL spectrum and ultraviolet-visible absorption spectrum of InP/ZnS green-emitting QDs and InP/ZnSe/ZnS red-emitting QDs respectively. We have tested the UV-visible absorption spectrum and PL spectrum of the InP/ZnS green-emitting QDs/toluene solution, as shown in figure 3 (a), we can see that the InP/ZnS green-emitting QDs has an absorption peak at 433 nm and the emission peak is 472 nm, the illustration shows InP/ZnS green-emitting QDs/toluene solution under UV irradiation. Figures 3 (b) and 3 (c) are the UV-visible absorption spectrum and PL spectrum of the InP/ZnSe/ZnS red-emitting QDs/octane solution before and after the emission peak position changes, respectively. It can be seen that before changing the emission peak position, the InP/ZnSe/ZnS red-emitting QDs has an absorption peak at 576 nm and the emission peak is 606 nm; after changing the position of the emission



**FIGURE 3.** (a) UV-visible absorption / PL spectrum of InP/ZnS green-emitting QDs / toluene solution. The illustration shows InP/ZnS green-emitting QDs / toluene solution under UV irradiation. (b) UV-visible absorption / PL spectrum of InP/ZnSe/ZnS red-emitting QDs / octane solution before peak position change (c) UV-visible absorption / PL spectrum of the InP/ZnSe/ZnS red-emitting QDs / octane solution after the peak position is changed. The illustration shows InP/ZnSe/ZnS red-emitting QDs/octane solution under UV irradiation.

peak, the InP/ZnSe/ZnS red-emitting has an emission peak at 611 nm and a red shift of 5 nm occurs. The illustration shows InP/ZnSe/ZnS red-emitting QDs/octane solution under UV irradiation. The red shift is similar to the red shift observed in semiconductors, which can be attributed to the changes in conduction band and valence band depending on the temperature expansion of the crystal lattice [18], [20].

## C. ELECTROLUMINESCENT PROPERTIES OF QDs

As shown in figure 4, in the previous work, we prepared WLED I using InP/ZnSe/ZnS red-emiting QDs with an



**FIGURE 4.** (a) EL spectrum of WLED I, the illustration shows the state of WLED I under natural light and the state of light emission in the dark (b) shows the color coordinates of WLED I (c) EL spectrum of WLED II prepared, the illustration is The state of WLED II in natural light and the state of emitting light in the dark (d) shows the color coordinates of WLED II.

emission peak of 606nm according to the method described above. Under the drive current of 5mA, we obtained the best electroluminescence performance. The relevant parameters are as follows: CRI is 90.3 (figure 4 (a)), chromaticity coordinates are  $(x = 0.3393, y = 0.3342)$  (figure 4 (b)), the light effect is 15.56 lm/W and the CCT is 5186K. The illustration shows the light emission of the WLED I device under 5mA driving current.

For comparison, according to the preparation method described above, we prepared WLED II using InP/ZnSe/ZnS red-emiting QDs with an emission peak of 611nm. Under the drive current of 20mA, we obtained the best electroluminescence performance. The relevant parameters are shown in figure 4 (c), the CRI is 91.0 (Figure 4 (c)), and the chromaticity coordinate is  $(x = 0.3365, y = 0.3334)$  (Figure 4 (d)) the light effect is 35.99 lm/W and the CCT is 5313k. The light emission of WLED II at 20mA can be seen in the illustration. By comparing the best electroluminescence performance of the WLED I device and the WLED II device, it can be seen that after the InP/ZnSe/ZnS red-emitting QDs emission peak is red-shifted by 5 nm, the maximum CRI of the WLED device increases by 0.7, the light effect is increased by 20.43 lm/w, and maintains a good color coordinate close to standard white light. At the same time, CCT can be seen closer to sunlight. According to the experimental data, this is because the average value of the color rendering indexes R1 to R8 of the WLED II device is larger than that of the WLED I device. And the R9 of the prepared WLED I device is 62, and after improving the emission peak position of InP/ZnSe/ZnS red-emitting QDs to 611nm, the R9 of the prepared WLED II device is 72, which has higher red color rendering.

As shown in figure 5, the EL spectra of the WLED I and WLED II devices as a function of drive current were also measured. It was found that the blue light emission peaks of WLED I and WLED II devices did not shift with the increase of the driving current. The emission peaks of green light and red light have only slightly red shifted.



**FIGURE 5.** (a) EL spectrum of WLED I with increasing drive current (b) EL spectrum of WLED II device with increasing drive current.

At the same time, we also conducted a study on the dependence of CRI on current. As shown in figure 6, it can be found that the CRI of the WLED II device is higher than that of the WLED I device. For WLED I devices, as the drive current increases to 350 mA, the CRI decreases to 89; For WLED II devices, as the drive current increases to 350mA, CRI has



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**FIGURE 6.** Comparison of CRI of WLED I and WLED II devices with driving current.

been maintained above 90, and the maximum value is 91, which is higher than that of WLED I devices. This shows that improving the peak position of InP/ZnSe/ZnS red-emitting QDs on the one hand enhances the color rendering of WLED devices and better restores the true color of objects; on the other hand, it improves the photoluminescence performance of the WLED device under high current and the situation where the electroluminescence performance is weakened. It has the potential to develop stable high-power devices.

The color coordinate distribution of the device is shown in figure 7. It was found that the CIE color coordinate distribution of the WLED I device along the black body radiation line continuously moved from the lower correlated color temperature to the higher correlated color temperature with the driving current from 5 mA to 350 mA (Figure 7 (a)), and the distribution of color coordinates of WLED I is very concentrated under the driving current of 5 mA ∼ 350 mA (Figure 7 (b)), only a slight movement occurs, and it is always located in the natural white light area, which is very suitable for daily lighting. It shows that after 5 nm red shift of the peak position of InP/ZnSe/ZnS red-emitting QDs, the red spectral component increases, which improves the stability of the color coordinates of the device under high current operation.



**FIGURE 7.** (a) Color coordinate distribution of WLED I device as a function of driving current (b) Color coordinate distribution of WLED II device as a function of driving current.

In summary, it can be found that improving the peak position of the InP/ZnSe/ZnS red-emitting QDs can produce

WLEDs with higher color rendering index and better color coordinates. And it still maintains excellent luminous performance under high current, which proves its potential in the development of stable high-power device applications.

#### D. AGEING TEST OF WLED

In order to further verify the practical application of the prepared WLED device, we also performed a 30-day aging test on it [21], [22]. We prepared multiple devices and placed them in the test conditions: a constant temperature and humidity box with 25  $°C$ , 85 % RH and a natural environment. Take out the samples every 24 hours. The length of the sample removal test should not exceed 30 minutes, to avoid the influence of temperature and humidity in the environment.

Figure 8 shows changes in EL spectrum, CRI, and light conversion efficiency of the prepared WLED device within 30 days, and the test current was 20 mA. As shown in figure 8 (a), over time, the spectral area of WLED devices in the natural environment decreases sharply on the first day of aging, and then decreases steadily, as shown in figures 8 (c) and (d). The CRI and light conversion efficiency of WLED devices in the natural environment also decrease sharply on the first day of aging, and then slowly decrease; as shown in figure 8 (b), WLED devices placed in a constant temperature and humidity box at 25  $\degree$ C and 85% RH, at the beginning, the spectral area of the device slowly rises, and then the spectral area gradually decreases. As shown in figures 8 (c) and (d), WLED devices placed in a constant temperature and humidity box at  $25^{\circ}$ C and  $85\%$  RH initially increased of the light conversion efficiency and CRI, and then slowly decrease. The reason why the WLED device placed in a constant temperature and humidity box at 25  $°C$  and 85% RH at first started to increase the spectral area and light conversion efficiency is that the QDs were eroded by water and oxygen, the QDs were destroyed, the emission intensity decreased, and the absorption is also reduced to a certain extent, and the reabsorption of the emitted light is reduced,



**FIGURE 8.** (a) EL spectrum of WLED device within 30 days under natural environment (b) EL spectrum of WLED device within 30 days under 25 ◦C and 85 %RH environment (c) comparison of the CRI of the device under natural environment and 25 ◦C, 85 %RH environment within 30 days (d) comparison of light conversion efficiency of the device under natural environment and 25 ◦C, 85 %RH environment within 30 days.

so that more light of other colors is transmitted out [23]–[27], the spectral area and the light conversion efficiency increased due to the increase in transmittance.

According to the comparison between the WLED device at the beginning and 30 days after aging at 25  $°C$ , 85% RH and the natural environment, respectively. It can be seen from the EL spectrum of the device that under the conditions of 25 ◦C and 85% RH, after a 30-day aging test, the green-emiting QDs have basically failed, and the red-emitting QDs have not completely failed due to the reabsorption of the yellow phosphor. After 30 days of aging experiments, the CRI has only decreased by 0.5 and the light conversion efficiency has decreased by 5.81 lm/w; In the WLED device quantum dots under natural conditions, it can be seen that both the red-emiting QDs and green-emiting QDs have failed, and their CRI has decreased by 5.4, and the light conversion efficiency has decreased by 15.19 lm/w.

In summary, it can be concluded that the WLED device prepared after improving the emission peak position of red-emitting QDs to 611 nm not only has high CRI and good color coordinates, but also maintains stability in color rendering performance in high humidity environments.

# **IV. CONCLUSION**

In this paper, we fabricated InP/ZnS green-emitting QDs and InP/ZnSe/ZnS red-emitting QDs with an emission peak at 611 nm, and combined with YAG:  $Ce^{3+}$  phosphor to produce WLED II device with high CRI. Compared with WLED I (the difference between WLED I and WLED II lies in the use of InP/ZnSe/ZnS red-emitting QDs with an emission peak position of 606 nm), WLED II shows high color rendering performance and stable working performance. The CRI of the WLED device was increased to 91.0, the CIE chromaticity coordinates were (0.3365, 0.3334), and the CCT was 5313 K. The effect of driving current on WLED I and WLED II devices in the range of 5 mA  $\sim$  350 mA was studied, and the results showed that after improving the peak position of InP/ZnSe/ZnS red-emitting QDs, the problems of rapid decline of CRI and large change of color coordinates under high current were improved. It can also be seen from the aging test that the prepared WLED device has potential for development in high humidity environments.

#### **REFERENCES**

- [1] Y. G. Soskind, J. A. Campin, M. D. Hopler, and G. H. Pettit, ''Solid state lighting and photobiological safety,'' *Proc. SPIE*, vol. 6426, Mar. 2007, Art. no. 64262C.
- [2] X. Wang, W. Li, and K. Sun, "Stable efficient CdSe/CdS/ZnS core/multishell nanophosphors fabricated through a phosphine-free route for white light-emitting-diodes with high color rendering properties,'' *J. Mater. Chem.*, vol. 21, no. 24, pp. 8558–8565, 2011.
- [3] H. Wang, K.-S. Lee, J.-H. Ryu, C.-H. Hong, and Y.-H. Cho, ''White light emitting diodes realized by using an active packaging method with CdSe/ZnS quantum dots dispersed in photosensitive epoxy resins,'' *Nanotechnology*, vol. 19, no. 14, Apr. 2008, Art. no. 145202.
- [4] C. Shen and L. Ke, "High color rendering index WLED based on YAG: Ce phosphor and CdS/ZnS core/shell quantum dots,'' *Proc. SPIE*, vol. 7516, Oct. 2009, Art. no. 751609.
- [5] C.-Y. Shen, K. Li, Q.-L. Hou, H.-J. Feng, and X.-Y. Dong, ''White LED based on YAG : Ce, Gd phosphor and CdSe–ZnS core/shell quantum dots,'' *IEEE Photon. Technol. Lett.*, vol. 22, no. 12, pp. 884–886, Jun. 15, 2010.
- [6] S. Chandramohan, B. D. Ryu, H. K. Kim, C. H. Hong, and E. K. Suh, ''Trap-state-assisted white light emission from a CdSe nanocrystal integrated hybrid light-emitting diode,'' *Opt. Lett.*, vol. 36, no. 6, pp. 802–804, 2011.
- [7] X. Peng, ''Low-cost and high-color-quality white light emitting diodes based on CdSe/ZnS quantum dots,'' *J. Opt.*, vol. 44, no. 3, pp. 249–254, Sep. 2015.
- [8] W.-S. Song, S.-H. Lee, and H. Yang, ''Fabrication of warm, high CRI white LED using non-cadmium quantum dots,'' *Opt. Mater. Express*, vol. 3, no. 9, pp. 1468–1473, 2013.
- [9] J. Ziegler, S. Xu, E. Kucur, F. Meister, M. Batentschuk, F. Gindele, and T. Nann, ''Silica-coated InP/ZnS nanocrystals as converter material in white LEDs,'' *Adv. Mater.*, vol. 20, no. 21, pp. 4068–4073, Nov. 2008.
- [10] P.-H. Chuang, C. C. Lin, and R.-S. Liu, "Emission-tunable CuInS2/ZnS quantum dots: Structure, optical properties, and application in white lightemitting diodes with high color rendering index,'' *ACS Appl. Mater. Interfaces*, vol. 6, no. 17, pp. 15379–15387, Sep. 2014.
- [11] X. T. Feng, F. Zhang, Y. L. Wang, Y. Zhang, Y. Z. Yang, and X. G. Liu, ''Luminescent carbon quantum dots with high quantum yield as a single white converter for white light emitting diodes,'' *Appl. Phys. Lett.*, vol. 107, no. 21, Nov. 2015, Art. no. 213102.
- [12] J. P. Park and S.-W. Kim, ''Surface stabilized InP/GaP/ZnS quantum dots with Mg ions for WLED application,'' *J. Nanosci. Nanotechnol.*, vol. 16, no. 5, pp. 5312–5315, May 2016.
- [13] C.-C. Hsiao, Y.-S. Su, and S.-R. Chung, "Fabrication of CuInS2/ZnS quantum dots-based white light-emitting diodes with high color rendering index,'' *Proc. SPIE*, vol. 10378, Sep. 2017, Art. no. 103780L.
- [14] F. Li, L. You, C. Nie, Q. Zhang, X. Jin, H. Li, X. Gu, Y. Huang, and Q. Li, ''Quantum dot white light emitting diodes with high scotopic/photopic ratios,'' *Opt. Express*, vol. 25, no. 18, p. 21901, 2017.
- [15] D. Li, J. Bai, T. Zhang, C. Chang, X. Jin, Z. Huang, B. Xu, and Q. Li, "Blue quantum dot light-emitting diodes with high luminance by improving the charge transfer balance,'' *Chem. Commun.*, vol. 55, no. 24, pp. 3501–3504, Mar. 2019, doi: 10.1039/C9CC00230H
- [16] T. Yuan, F. Yuan, X. Li, Y. Li, L. Fan, and S. Yang, "Fluorescencephosphorescence dual emissive carbon nitride quantum dots show 25% white emission efficiency enabling single-component WLEDs,'' *Chem. Sci.*, vol. 10, no. 42, pp. 9801–9806, 2019.
- [17] M. D. Tessier, D. Dupont, K. De Nolf, J. De Roo, and Z. Hens, "Economic and size-tunable synthesis of  $InP/ZnE$  ( $E = S$ ,  $Se$ ) colloidal quantum dots," *Chem. Mater.*, vol. 27, no. 13, pp. 4893–4898, Jul. 2015.
- [18] Y. Kim, S. Ham, H. Jang, J. H. Min, H. Chung, J. Lee, D. Kim, and E. Jang, ''Bright and uniform green light emitting InP/ZnSe/ZnS quantum dots for wide color gamut displays,'' *ACS Appl. Nano Mater.*, vol. 2, no. 3, pp. 1496–1504, Mar. 2019.
- [19] F. Cao, S. Wang, F. Wang, Q. Wu, D. Zhao, and X. Yang, "A layer-bylayer growth strategy for large-size InP/ZnSe/ZnS core–shell quantum dots enabling high-efficiency light-emitting diodes,'' *Chem. Mater.*, vol. 30, no. 21, pp. 8002–8007, 2018.
- [20] J. Tang, F. Li, G. Yang, Y. Ge, Z. Li, Z. Xia, H. Shen, and H. Zhong, ''Reducing the chromaticity shifts of light-emitting diodes using gradientalloyed Cd*x*Zn1−*x*Se*y*S1−*<sup>y</sup>* ZnS core shell quantum dots with enhanced high-temperature photoluminescence,'' *Adv. Opt. Mater.*, vol. 7, no. 10, pp. 1801687.1–1801687.9, 2019.
- [21] S. S. B. Nasir, A. Tanaka, S. Yoshiara, and A. Kato, ''Luminescence properties of  $Li_2SrSiO_4$ :  $Eu^{2+}$  silicate yellow phosphors with high thermal stability for high-power efficiency white LED application,'' *J. Lumin.*, vol. 207, pp. 22–28, Mar. 2019.
- [22] B. Xie, Y. Cheng, J. Hao, X. Yu, W. Shu, K. Wang, and X. Luo, ''White light-emitting diodes with enhanced efficiency and thermal stability optimized by quantum dots-silica nanoparticles,'' *IEEE Trans. Electron Devices*, vol. 65, no. 2, pp. 605–609, Feb. 2018.
- [23] S. R. Cordero, P. J. Carson, R. A. Estabrook, G. F. Strouse, and S. K. Buratto, ''Photo-activated luminescence of CdSe quantum dot monolayers,'' *J. Phys. Chem. B*, vol. 104, no. 51, pp. 12137–12142, Dec. 2000.
- [24] W. G. J. H. M. van Sark, P. L. T. M. Frederix, A. A. Bol, H. C. Gerritsen, and A. Meijerink, ''Blueing, bleaching, and blinking of single CdSe/ZnS quantum dots,'' *ChemPhysChem*, vol. 3, no. 10, pp. 871–879, Oct. 2002.
- [25] M. Jones, J. Nedeljkovic, R. J. Ellingson, A. J. Nozik, and G. Rumbles, ''Photoenhancement of luminescence in colloidal CdSe quantum dot solutions,'' *J. Phys. Chem. B*, vol. 107, no. 41, pp. 11346–11352, Oct. 2003.
- [26] M. C. Mancini, B. A. Kairdolf, A. M. Smith, and S. Nie, ''Oxidative quenching and degradation of polymer-encapsulated quantum dots: New insights into the long-term fate and toxicity of nanocrystals *in vivo*,'' *J. Amer. Chem. Soc.*, vol. 130, no. 33, pp. 10836–10837, Aug. 2008.
- [27] J. Müller, J. M. Lupton, A. L. Rogach, J. Feldmann, D. V. Talapin, and H. Weller, ''Air-induced fluorescence bursts from single semiconductor nanocrystals,'' *Appl. Phys. Lett.*, vol. 85, no. 3, pp. 381–383, Jul. 2004.



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