Liquid-type AgInS₂/ZnS quantum dot-based warm white light-emitting diodes

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Abstract: We here report a warm white light-emitting diode (WLED) by employing the red-emitting liquid layer of AgInS₂/ZnS quantum dots (QDs) over the yellow-emitting YAG:Ce phosphor-based WLEDs. Compared to the commercial WLEDs, our liquid-type QD-WLEDs exhibit a color temperature of 3500K and an improved color rendering index of 85. In addition, the experimental results indicate that the liquid structure warm white light device has a higher luminous efficiency of 72.1 lm/W and a better color stability against the extended working time in comparison to the solid-type QD-WLEDs.

Key words: AgInS₂/ZnS; quantum dot; liquid-type; white light-emitting diodes

1. Introduction

Among solid-state lighting technology, phosphor-converted white light-emitting diodes (pc-WLEDs) have received extensive attention owing to their low power consumption, environmental friendliness, small size, long operation lifetime, thus, they are gradually replacing the traditional incandescent and fluorescent bulbs [1-5]. However, these pc-WLEDs typically have a low color rendering index (CRI) because of the lack of the red spectral component [6-10]. In addition, these micron-sized phosphors have a scattering effect making pc-WLEDs usually have a low device luminous efficacy [7,11,12]. So semiconductor quantum dots (QDs) based WLEDs have been developed because of their excellent properties, such as tunable absorption and emission, quantum-confinement effect, high quantum yield (QY) and easy chemical synthesis process [13-16]. Moreover, highly fluorescent QDs with adequately small size can also avoid light scattering [17-19].

As a display backlight source and indoor lighting, high-efficiency QD-WLED with high color rendering index (CRI) values of 90.1 has been fabricated by combining a blue InCaN LED chip with $\text{Sr}_3\text{SiO}_5\text{:Ce}^{3+}/\text{Li}^+$ phosphor and red-emitting CdSe QDs [12]. Meanwhile, QD-WLEDs using YAG:Ce, Cd phosphor and CdSe/ZnS core/shell QDs or CdS/ZnS:Cu QDs as light converting components, were also fabricated and exhibited device luminous efficiencies of 80 lm/W and 46.5 lm/W, respectively [20,21]. However, these traditional solid-state QD-WLEDs have a thermal effect and a lower stability. What is more, the quantum efficiency is usually reduced when the solvent is dried up due to the self-aggregation effect [22,23]. In order to improve the device performance, liquid-type QD-WLED has been proposed with the luminous efficiency and the CRI of 271 lm/W_{opt} and

95, respectively [24]. Nevertheless, the liquid-type device was fabricated using the CdSe QDs. The presence of the toxic Cd element is detrimental to humans and the environment [8,20,25-27]. Therefore, Cd-based QDs have been replaced by non-Cd compositions such as binary III–V (InP) compounds, ternary I–III–VI (CuInS₂, CuInSe₂, AgInS₂) compounds and carbon dots [28-31].

In this study, a solid- and liquid-type white QD-WLEDs were fabricated using AgInS₂/ZnS (AIS/ZnS) QDs. Compared to II-VI type CdSe and III-V type InP QDs, I-III-VI type AgInS₂ (AIS) QDs exhibit high absorption coefficients, large Stokes shifts and broad emission bandwidth (typically >100 nm) [32,33], which is suitable as a single color-converting material in the WLED packages due to the broad spectral coverage [30,34]. Furthermore, in order to ensure the quantum efficiency of AIS/ZnS QDs and improve the device stability, we fabricated a glass container to contain the QD solution and to avoid the volatilization of the solvent. In this way, we got a high luminous efficiency liquid-type warm QD-WLED.

2. Experimental section

2.1 Materials

Indium (III) acetylacetonate (In(acac)₃, 99.99%), silver nitrate (AgNO₃, 99.9995%), zinc stearate (12.5–14% Zn basis), oleic acid (OA, 90%) and 1-octadecene (ODE, 90%) were purchased from Alfa Aesar. Sulfur powder (S, 99.98%) and trioctylphosphine (TOP, 90%) were purchased from Sigma-Aldrich. Dodecanethiol (DDT, 98%) and oleylamine (OLA, 80-90%) were purchased from Aladdin. YAG:Ce phosphor was purchased from InterMatrix

(Shenzhen, China). Blue InLED chips ($\lambda_{\text{max}}=455\text{nm}$) were purchased from Epileds (Shenzhen, China). UV glue NOA60 was ordered from LIENHE Fiber Optics (Shanghai, China). All chemicals were used directly without further purification.

2.2 Synthesis of AIS/ZnS core/shell QDs

AIS/ZnS core/shell QDs with emission peaks of 640 nm were prepared according to literature [32,33]. AIS core QDs were synthesized firstly. 0.1 mmol of AgNO_3 (0.017 g), 0.5 mmol of $\text{In}(\text{acac})_3$ (0.21 g), 1.5 mmol of OA (0.47 mL) and 25 mmol of ODE (8.0 mL) were added into a 100 mL three-neck flask. The reaction mixture was degassed under vacuum for 20 min at room temperature. The solution was heated to 90°C to form a clear solution, then 4.0 mmol of DDT (1.0 mL) was added to the reaction flask. Subsequently, the reaction solution was heated to 150°C . A S-OLA solution (0.8 mmol of sulfur powder (0.026 g) dissolved in 4 mmol OLA (1.3 mL)) was quickly injected into the reaction solution for 5 min. By changing the reaction time, AgInS_2 core QDs with different emission wavelengths were obtained.

For the ZnS shell overcoating, a ZnS shell solution was needed. 0.4 mmol of Zn stearate (0.25 g) and 0.4 mmol of S powder (0.013 g) were dissolved in 8 mmol of TOP (4 mL) in a 25 mL three-neck flask. Then the solution was degassed for 20 min at ambient temperature. Next, the reaction solution was heated to 100°C under nitrogen flow until a clear colorless solution formed. Afterward, the mixed solution was quickly injected into the above-prepared AgInS_2 core solution at 150°C and maintained for 30 minutes. Then 10 mL toluene was quickly injected into the solution to quench the reaction. At last, the final solution was cooled

to room temperature and purified by adding excess anhydrous ethanol. The flocculent precipitate was centrifuged at 5000 rpm for 5 min and the supernatant was decanted. This precipitation process was repeated at least three times and the final precipitate was dispersed in hexane.

2.3 Fabrication of QD-WLEDs

The solid- and liquid-type QD-WLEDs were fabricated at the same time for comparison. Blue InGaN LED chips with the emission peak wavelength centered at 455 nm were used as an excitation source for the fabrication of WLEDs. A certain amount of yellow YAG:Ce phosphors was dispersed in the UV glue and sonicated for 10 min to form a homogeneous mixture. Then the mixture was coated onto the InGaN LED chip. The device was then cured with a UV-lamp for 1 min. In order to get a high luminous efficiency warm WLED, the prepared red-emitting AIS/ZnS core/shell QD solution having an optical density (OD) of 8 at 480 nm were mixed with the UV glue to get a uniform solution. The final red AIS/ZnS QD pastes were dispensed onto the YAG:Ce-based WLED chip and cured with a UV-lamp to get a solid-type QD-WLED.

For the fabrication of liquid-type WLEDs, the prepared AIS/ZnS QDs dispersed in hexane with an absorbance of 5.0 at 480 nm was injected into a glass container. Fig.1 (e) illustrates the process of making the glass container. At first, a few glass slides of 0.1 cm thickness were cut into 1.6 cm×1.6 cm (2 pieces, marked as A and B in Fig. 1), 1.6 cm×0.3 cm (2 pieces, C and D), 1.0 cm×0.3 cm (1 piece, E) and 0.9 cm×0.3 cm (1 piece, F), respectively. Secondly, the four narrow strips were sandwiched in between the two large

square pieces of glass with silicon sealant, and a very narrow gap (0.1 cm, the needle position) was left for the injection of the QD solution. Finally, the gap was sealed with an epoxy-based glue to avoid the volatilization of the QD solution. The overall volume which can accommodate the QD solution was $1.0 \text{ cm} \times 1.0 \text{ cm} \times 0.1 \text{ cm} = 0.1 \text{ cm}^3 = 0.1 \text{ ml}$. Both the solid- and liquid-type devices were fabricated with the same QD and characterized under the same ambient conditions and the same excitation light source (the 455 nm InGaN LED chips).

Fig. 1 The process of making the glass container

2.4 Characterizations

The absorption spectra of the AIS/ZnS QD samples were measured by using a Shimadzu 3600 UV-Vis spectrophotometer. Photoluminescence (PL) spectra of AIS QDs and the emission spectra of the devices were obtained by a Zolix Omni- λ 300 luminescence spectrometer. PEI Tecnai F20 transmission electron microscope (TEM) was used to characterize the morphology and size of the QDs. Powder X-ray diffraction (XRD) was carried out on D8 Advance Bruker-AXS. The optical properties of the AIS-based liquid- and solid-type QD-WLEDs, such as color rendering index (CRI), correlated color temperature (CCT) and color coordinates (CIE) were evaluated in software of Spectra Win. Their

illumination was measured by an AS823 Digital Lux Meter. The fluorescence quantum yields (QY) of solid and liquid AIS/ZnS QDs were measured by the same spectrometer using an integrating sphere with its inner face coated with BENFLEC[®]. AIS/ZnS QD solution was diluted to measure quantum yield at very low concentration. The solid QDs were measured by spin-coating the homogeneous mixture of AIS/ZnS QDs and UV glue on the glass sheet.

3. Results and discussion

Fig. 2 (a) shows the absorption and photoluminescence (PL) spectra of AIS/ZnS QDs with different emissive wavelength. The emission peaks of a series AIS/ZnS QDs were 600 nm, 620 nm, 640 nm and 660 nm, respectively. The QY of solid and liquid 640nm AIS/ZnS QDs were confirmed to be 37% and 51%, respectively. This result shows that the liquid AIS/ZnS QDs have a higher QY than that of the solid one. It is noted that AIS/ZnS QDs have a large Stokes shift that is beneficial to eliminate the self-absorption and to generate a high color rendering WLED.[35] As shown in the TEM and HR-TEM images of the 640 nm AIS/ZnS QDs in Fig. 2 (b). From the TEM observation, the AIS/ZnS QDs were monodispersed and spherical in morphology. The HR-TEM images also indicate that the average size of AIS/ZnS QDs is 5.2 nm. In addition, the clear lattice fringe in the HR-TEM images of the AIS/ZnS QDs indicates that the AIS/ZnS particles have well-crystallized structures. Fig. 2 (c) shows the XRD patterns of AIS/ZnS QDs. Four XRD peaks were observed in XRD patterns. The first one is the peak of quartz substrates. The next three peaks positioned at 2θ values of 27.3° , 45.8° and 53.5° , which were assigned to (311), (203) and (620) planes of the cubic structure, respectively. The result is consistent with the literature reported previously.

Fig. 2 (a) Absorption and PL emission spectra of AIS/ZnS QDs with different emissive wavelengths excited at 405 nm; (b) TEM and HR-TEM images of 640 nm AIS/ZnS QDs; (c) XRD patterns of AIS/ZnS QDs.

Fig. 3 (a) depicts the output spectra of the liquid-type QD-WLEDs with different emissive wavelength AIS/ZnS QDs (600, 620, 640, 660 nm), and the optical parameters of these four devices are listed in Table 1. It is noted that 640 nm AIS/ZnS QD based liquid-type WLED was superior to other QDs in most performance: a lower color temperature and higher CRI and luminous efficiency. As shown in Table 1, it is found that the luminous efficiency of devices decrease with the increasing of emission wavelengths of AIS/ZnS QDs, which is mainly attributed to a strong emission tail beyond 650 nm and a low eye sensitivity function to red light. However, the 640 nm AIS/ZnS QDs based WLED still has a good luminous efficiency of 72.1 lm/W. In addition, the spectra of YAG: Ce phosphor-based WLEDs is lack of emission in the range of 600-700 nm, which cause their poor CRI. In order to improve the

CRI of the WLEDs, we choose red-emitting AIS/ZnS QDs with a wide bandwidth to compensate the deficiency of red region. From the experimental results as shown in Table 1, we can see that WLEDs based on AIS/ZnS QDs with the emission peak of 640 nm have the improved CRI of 85, which is mainly because of the best compensation of device spectra. Above all, AIS/ZnS QDs with the emission peak of 640 nm were selected to fabricate the WLEDs. Fig. 3 (b) shows the output spectra of YAG:Ce based pc-WLED (black line), YAG:Ce with 640 nm AIS/ZnS QDs solid- (red line) and liquid-type WLEDs (green line). The spectrum of the solid-type WLED appeared a slight red shift compared with the liquid-type WLED, which was mainly caused by greater thermal effect of solid-type device due to the closer distance between QDs and LED chip. The CIE color coordinates of these three different types of devices are depicted in Fig. 3 (c). The color coordinate and the correlated color temperature (CCT) of the YAG:Ce phosphor based WLED were (0.348, 0.386) and 5125 K, respectively. However, by adding red emissive AIS QDs, the color coordinate and the color temperature of devices changed obviously. The CIE color coordinate of solid-type WLED moved to warm white light region (0.405, 0.362) and the correlated color temperature dropped to 3284 K. The color coordinate of liquid-type is (0.399, 0.379) that located on the Planckian locus and the color temperature was 3573 K. It has turned warm white light (CCT = 2580-3710 K).

The optical properties of these seven devices operated at 20 mA are summarized in Table 1. Due to the compensation of red spectral region by adding red-emitting AIS/ZnS QDs, the dual phosphors (YAG:Ce and AIS/ZnS QDs) WLEDs showed an improved CRI of 85 compared with the single phosphor (YAG:Ce) WLEDs (CRI = 69). In addition, the luminous

efficiency of dual phosphors WLEDs ($LE = 61.5$ and 72.1 lm/W for the solid- and liquid-type WLEDs, respectively) exhibits a slight decline compared with the single phosphor WLEDs ($LE = 87.4$ lm/W), which is a reasonable result due to the scattering of more photons for the dual phosphors device [36].

Fig. 3 (a) The output spectra of the liquid-type QD-WLEDs with different emissive wavelength AIS/ZnS QDs (600, 620, 640, 660 nm); (b) The output spectra of single phosphor (YAG:Ce) based WLED (black line), dual phosphors (YAG:Ce and 640 nm AIS/ZnS QDs) based solid-type WLED (red line) and liquid-type WLED (green line); (c) CIE color coordinate diagram of the three devices.

Table 1. The parameters of seven devices operated at 20 mA

Device	CCT (K)	CIE (x, y)	CRI	LE (lm/W)
YAG+600nm Liquid QD	4811	(0.351, 0.388)	73	79.7
YAG+620nm Liquid QD	4773	(0.352, 0.388)	78	75.3
YAG+640nm Liquid QD	3573	(0.399, 0.379)	84	72.1
YAG+660nm Liquid QD	3438	(0.407, 0.399)	79	67.9
YAG	5125	(0.348, 0.386)	69	87.4

YAG+640nm Solid QD	3284	(0.405, 0.362)	85	61.5
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Note. CCT: color temperature, CIE: color coordinates (x, y), CRI: color rendering index, LE: luminous efficiency.

The structure and the real emitting color pictures of these two types of devices operated at 300 mA are exhibited in Fig. 4 (a) and (b).

Fig. 4 (a) and (b) are the structure and emitting picture of the solid-type QD-WLED, respectively; (c) and (d) are the structure and the emitting picture of liquid-type QD-WLED, respectively; both WLEDs were operated at 300 mA.

Fig. 5 (a) and (b) show the output spectra of the solid- and liquid-type QD-WLEDs under the driving currents from 20 mA to 300 mA. It was noted that the emissive peak position of the liquid-type WLED remained the same, but the emissive peak of AIS/ZnS QDs appeared a slight redshift for the solid-type WLED, which was mainly caused by QD agglomeration due to the low QD solubility in the UV glue [37]. We calculated the CRI and CIE color

coordinates of these two devices under different driving currents. The variations of CRI and CIE color coordinates were larger for the solid device. This result demonstrated the liquid device had a better stability when the forward current increased continuously. The CIE color coordinates of solid- and liquid-type WLEDs at 20-300 mA were revealed in Fig. 5 (c). Apparently, the CIE color coordinates of these two devices all appeared blue shift with increasing currents, which is consistent with the results of previous QD-LEDs [18,38]. But the solid-type device (blue hollow circle) has more obvious change with the injection current increase compared with the liquid-type device (red hollow circle). It is attributed to the thermal quenching of AIS/ZnS QDs induced by the increased temperature of LED chip surface at higher driving current for traditional solid-type WLED, which leads to the decline of PL QY of AIS/ZnS QDs [38-40]. Nevertheless, the influence of thermal effect was lesser for the liquid-type WLED. Fig. 5 (d) exhibits the change of the luminous efficiency of two types of devices with the increase of injection current. The maximum luminous efficiency for the solid- and liquid-type QD-WLEDs were 61.5 lm/W and 72.1 lm/W at a driving current of 20 mA, respectively. The luminous efficiency of two types of devices all decreased as the forward current changed from 20 mA to 300 mA, which is mainly caused by the efficiency decline of the LED chip [41]. In addition, the saturation of QD emission with increasing forward currents also caused the decline of luminous efficiency of devices [42]. However, the rate of decline of the solid-type device was faster than the liquid-type device. The data illustrated that the liquid-type QD-WLEDs not only had a superior stability but also a higher luminous efficiency.

Fig. 5 Output spectra of the AIS/ZnS QD solid- (a) and liquid-type (b) WLEDs at different injection currents of 20 mA to 300 mA; (c) Variations of CIE color coordinates for solid-type device (blue hollow circle) and liquid-type device (red hollow circle) under different driving currents of 20 mA to 300 mA; (d) luminous efficiency of solid- (black line) and liquid-type QD-WLED (red line) at different forward currents of 20 mA to 300 mA.

We further investigated the stability of these two types of devices. Firstly, the glass container filled AIS/ZnS QD solution was sealed to avoid volatilization of its solvent and also to prevent water and oxygen from reacting with the QDs. In this way, the QY of the QDs can be preserved over a long period of time. Fig. 6 (a) and (b) show the output spectra of the solid- and liquid-type QD-WLEDs under different working time. It was noted that the emission intensity of these two QD-WLEDs all decreased slightly when the devices were lightened at a driving current of 300 mA, whereas the intensity of the solid-type white light device decreased faster, which was mainly due to the increased temperature on the surface of blue

chips. The CIE color coordinates and color temperatures also changed slightly with longer working time. The variations of luminous efficiency for these two devices with increasing working time are shown in Fig. 6 (c). Apparently, the luminous efficiency of these two devices all decreased with the working time from 0 to 1000 hours. Moreover, the efficiency reductions of the solid- (black line) and liquid-type (red line) structure are 61% and 8% after 1000 hours of storage, respectively. Fig. 6 (d) exhibits the shifts of the color rendering index for solid-type (black line) and liquid-type (red line) QD-WLEDs from 0 to 1000 hours. It is found that the color rendering index of solid-type structure had a slight variation. However, the liquid-type device was few changed. From what has been discussed above, we can conclude that the liquid-type QD-WLED has a better stability than the solid-type QD-WLED.

Fig. 6 (a) and (b) Output spectra of the solid- and liquid-type QD-WLED at different working time (0-5 hours), respectively; Variations of (c) luminous efficiency and (d) CRI for the solid- (black line) and liquid-type QD-WLEDs (red line) at different working time.

4. Conclusion

In conclusion, the red-emitting AIS/ZnS QDs is an excellent choice to compensate the lack of red spectral component of commercial YAG:Ce phosphor. Liquid-type QD-WLEDs were fabricated with the combination of red-emitting AIS/ZnS QDs and yellow-emitting YAG:Ce phosphor on blue InGaN LED chips. They exhibited a higher color rendering index (~ 85) and a lower color temperature (~ 3500 K) in comparison to the commercial YAG:Ce based WLEDs. Furthermore, liquid-type WLEDs exhibited higher luminous efficiency (72.1 lm/W at driving current of 20 mA) and more stable CIE color coordinate than the solid-type WLEDs with the same QD/YAG:Ce combination.

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Graphical Abstract

An improved luminous efficiency and enhanced stability for the white light-emitting diode was achieved due to the new device structure.