

Optical Properties of Cd-Free Quantum Dots-Based Fluorescent Film

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Abstract. CuInS₂/ZnS Cd-free quantum dots (QDs) have many characteristics, such as high quantum yield (QY), wide emission peak and adjustable light color. They are suitable for optical conversion materials and applied in solid-state lighting (SSL). However, they are not easily dispersed during encapsulation, resulting in the deviation of light color out of the white light area after encapsulation. In this study, we use thermal injection synthesis method to prepare CuInS₂/ZnS and CuInS₂/ZnS:Al QDs. In order to improve the dispersion of QDs, solution type of QD/PS-PE-BR-PS copolymer (SEBS) mixture was prepared by mixing QD and SEBS with different ratios (10, 20, and 30 wt%) to form a fluorescent film. The experimental results show that the emission wavelengths and QY of CuInS₂/ZnS and CuInS₂/ZnS:Al QDs are 533 nm, 84 % and 536 nm, 97 %, respectively. The emission wavelength of CuInS₂/ZnS-based fluorescent film is 574 nm, while CuInS₂/ZnS:Al-based fluorescent film is 582 nm. The CRI, luminous efficacy, chromaticity coordinates and correlated color temperature of 20 wt% CuInS₂/ZnS-based fluorescent film excited by blue chip is 64, 42 lm/W, (0.33, 0.32), and 5443 K, respectively. On the other hand, we find that the CRI of CuInS₂/ZnS:Al-based fluorescent film can be improved from 64 to 73, and the luminous efficacy is 51 lm/W.

1. Introduction

The white light-emitting diode (WLEDs) has attracted extensive attention in the solid-state lighting (SSL) and backlight source technology because of its advantages of environmentally friendly, energy saving, and so on [1-3]. In SSL, there are at least combine two wavelengths of light to form white light, such as the white light is formed by combination a blue InGaN with the yellow YAG: Ce³⁺ phosphor [4]. However, due to the color temperature is higher than 4500 K and the lacks of red emission spectrum, the color rendering index (CRI) of YAG-based WLED is less than 80, which limits the application of indoor lighting [5]. Compared with phosphor, most of quantum dots (QDs) especially for Cd-based QDs exhibit tunable photoluminescence spectrum and high quantum yield (QY) [6, 7]. Narrow full width at half maximum (FWHM) and easy adjustment of three basic colors (red, green and blue) of QDs make them quite suitable to be used as backlight source [8]. However, high CRI is the main demand for SSL. So, the more important thing is to extend the emission spectrum of luminescent materials to covers entire visible range. In fact, the YAG-based WLED which is more popular device that often improve CRI by blending Cd-based red-emissive QDs to enhance the red band intensity in EL spectrum. Because of the well-known toxicity, Cd-based QD will be limited in the future. As time goes on, composition tunable of InP [9] and I-III-VI alloyed QDs (CuInS₂ [10], CuInSe₂ [11] and AgInS₂ [12]) which is Cd-free materials has been developed, but the FWHM of InP



QD is not wider enough to application in WLED [13]. Today, the emission wavelength of I-III-VI alloyed QDs can be adjusted in the range from visible to near infrared by doping process. Among these I-III-VI QDs, CuInS_2 (CIS) is a very suitable one for SSL applications because of its excellent absorption coefficient at 450 nm and wide emission spectrum in yellow green range [14]. In particular, the QY of CIS QDs can be increased from 2 to more than 70 % by coating ZnS shell, and the FWHM is larger than 80 nm [15]. Although the CRI of CIS/ZnS QDs modified YAG-based WLED is ultrahigh (>90), the luminous efficacy (<40 lm/W) is still lower than that of conventional WLEDs [16-18] and the emission wavelength red-shifts very significantly [19, 11], due to the agglomeration between QDs and lower QY compared to YAG. Moreover, the compatibility between silicone and CIS/ZnS is also poor, resulting in QDs tends to agglomerate. Pinhua et al. reported that the luminous efficacy of device enhances by adding Al [20]. On the other hand, the package form and encapsulates are also the key factors for devices performance. Remote-typed of QD-based WLED was produces which meaning that a fluorescent film is made and without contact with the blue InGaN chip [16-18]. Here, we report a facial chemical route to synthesize CIS/ZnS:Al QDs with high QY (97 %) by oxide layer passivation. The compatibility of $\text{CuInS}_2/\text{ZnS:Al}$ QDs-based fluorescent films can be improved and luminous efficacy is 51 lm/W.

2. Experimental

2.1. Chemicals

Copper iodide (I) (CuI , 99.99 %), 1-dodecanethiol (DDT, 98 %), octadecene (ODE, 90 %), aluminum isopropoxide (Al(IPA)_3 , 99.9 %) and zinc stearate (Zn(SA)_2 , 10-12 % Zn basis) are provided by Aldrich. Indium acetate (In(AC)_3 , 99.99 %) was purchased from Alfa Aesar. Styrene block copolymer (SEBS, model 01082) is provided by Phon Tech Industrial Company. Toluene (99.5 %), hexane (99.7 %), acetone (99.9 %), methanol (99.7 %), and isopropanol (99.5 %) were used directly.

2.2. Synthesis

2.2.1. Synthesis of CuInS_2 quantum dots. The CIS core QDs are synthesized by the hot injection method. 0.0625 mmol CuI , 0.5 mmol In(AC)_3 and 5 ml DDT were added to the 100 ml three-necked flask and heated at 100 °C for 30 minutes in vacuum first and then purged with Ar to form a yellow-green solution. Subsequently, the mixture was heated to 230 °C under the heating rate of 15 °C/min, and the CIS QDs can be obtained after reacts for 5 minutes.

2.2.2. Synthesis of CIS/ZnS quantum dots. The core/shell structure of CIS/ZnS QD is synthesized as follows. ZnS stock solution was prepared by mixing 4 ml ODE, 1 ml DDT, and 8.3 mmol Zn(SA)_2 in the three-necked flask and heated to 190 °C, then reacted for 50 minutes under Ar atmosphere. After that, the ZnS stock solution dropped into the CIS core QD solution at about 1 ml/min rate. Then the mixture was heated to 240 °C and reacted for 120 minutes. The CIS/ZnS core/shell QD was purified by excess methanol, and the supernatant was removed and the precipitate was collected. The precipitates were then dispersed in toluene and precipitated with excess methanol, and repeated precipitation/dispersion cycles three times to remove the byproducts and unreacted precursors. Finally, the precipitate was purified by toluene/acetone/methanol (1:1:2) cosolvent and the purified QD was dried at room temperature.

2.2.3. Synthesis of CIS/ZnS:Al quantum dots. The synthesis process of CIS/ZnS:Al was the same with CIS/ZnS. 4.15 mmol Al(IPA)_3 was dissolved in DDT. The Al(IPA)_3 and ZnS solutions were injected into CIS core solution simultaneously at 240 °C and reacted for 120 minutes. The precipitate was purified with hexane/isopropanol (1:5) cosolvent, and the purified QD was dry at room temperature.

2.3. Preparation of fluorescent film and white LED

The QDs, toluene, and PS-PE-BR-PS copolymer (SEBS) were mixed together and the mixture poured into the mold to form fluorescent film with 0.6 mm thickness, as showed in figure 1 (a). The

fluorescent film putted on the top of blue LED to form white LED, as showed in figure 1 (b), and the performance of device is measured by integral sphere (Isuzu Optics, ISM-360) under 20 mA injection current.

2.4. Characterizations

The optical properties of the samples were measured by Fluorescence Spectrometer (Hitachi F-7000) and ultraviolet visible spectrometer (UV-vis, Hitachi UH 5300). The relative QY of the samples was determined by comparing the emission area of samples to the organic dye (Rhodamine 6G in methanol). The structure of samples was measurement by X-ray diffractometer (XRD, Bruker D8A25) with Cu K_{α} ($\lambda=1.5403$ Å). Transmission electron microscope (TEM, JEM-2100F) was used to analyze the morphologies and size distributions of the samples.

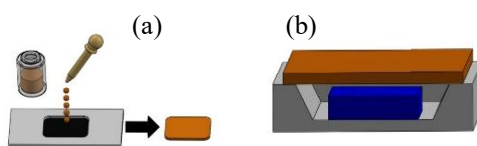


Figure 1. The schematic diagram of (a) fluorescent film and (b) fluorescent film-based WLED.

3. Results and Discussion

Figure 2 shows the excitation, emission and UV absorption spectra of CIS/ZnS and CIS/ZnS:Al QDs. In figure 2 (a), the absorption peak of CIS/ZnS QD is not obvious due to the multiple defect energy levels in QD. Moreover, the absorption peak of CIS/ZnS:Al QD, in figure 2 (b), is more prominent than that of CIS/ZnS QD. The FWHM of CIS/ZnS and CIS/ZnS:Al are 74 and 83 nm, respectively. This may be meaning that Al is doped into the CIS core, and produces a defect levels within the band gap, resulting in extends the FWHM. This is beneficial to increase the color rendering index (CRI) value of WLED. Both samples show the tail in UV absorption spectra meaning that the intrinsic character of defect emission mechanism [21]. Moreover, we also observe that a large Stokes shift and the wide FL emission range for both samples. The emission peaks of CIS/ZnS and CIS/ZnS:Al is 533 and 536 nm, respectively. The emission wavelengths of both samples are quite close, indicating that the doping of Al does not affect the band gap. We also can find that the QY can be enhanced from 84 to 97 % after Al doping, which might be due to the formation of Al_2O_3 on the surface, resulting in the passivation of the QDs surface more effective [20]. In figure 3 (a-c), the XRD pattern shows that the CIS QD has a chalcopyrite structure. With the coating of the ZnS shell, the main three diffraction peaks of CIS/ZnS move toward the ZnS zinc blende structure slightly. This displacement indicates the formation of $ZnCuInS_2$ alloy [21, 22], while the CIS/ZnS:Al diffraction peak is the same as CIS/ZnS, showing that a few amount of Al has little effect on the crystal structure. Based on figure 3 (d) and (e), we find that the particle size of CIS/ZnS:Al and CIS/ZnS are similar and about 3 nm. Moreover, the morphologies of samples are tetrahedral [20].

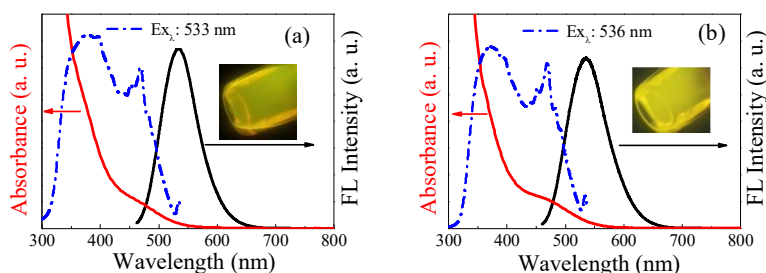


Figure 2. The absorption, excitation, and emission spectra of (a) CIS/ZnS and (b) CIS/ZnS: Al.

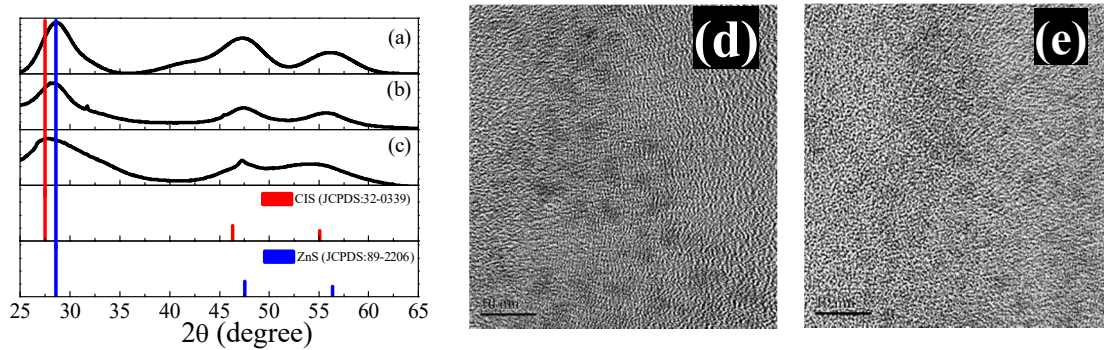


Figure 3. XRD patterns. (a) CIS/ZnS:Al, (b) CIS/ZnS, and (c) CIS. TEM images. (d) CIS/ZnS, (e) CIS/ZnS: Al.

A large amount of sulfenyl remains on the surface of the QDs, which makes the silicone gel unable to curing. Therefore, the SEBS copolymer, which is similar to silicone gel and it can be miscible with toluene and CIS QDs as well as the compatibility can be improved. Because the heat resistance of SEBS is about 140 °C, we use remote-typed to encapsulate it. In the package, we encapsulate the film with QD content of 10, 20, and 30 wt %, and make white light with two films assembly.

The EL spectra of CIS/ZnS- and CIS/ZnS:Al-based WLED are shown in figures 4 (a) and (b). We can find that the emission peak of CIS/ZnS:Al-based WLED is 584 nm, and the red-shift is about 50 nm. On the other hand, the emission wavelength of CIS/ZnS-based WLED is 573 nm, the red-shift is about 40 nm. The larger shift of CIS/ZnS:Al WLED may be due to the different residual precursors of the QDs. In addition, we can observe that the emission peak of CIS/ZnS:Al-based WLED does not change much by altering the content of QDs, and the difference between maximum and minimum emission peak is 4 nm, while the difference for CIS/ZnS-based WLED is 10 nm, illustrates that the dispersibility can be improved by Al doping, which change the surface properties of CIS/ZnS QDs.

Figures 4 (c) and (d) show the CIE coordinates of devices. The CIE of CIS/ZnS:Al-based WLED not change with QD concentrations and the correlated color temperature (CCT) is below 4500 K, and the highest luminous efficacy is 51 lm/W, while the CIE of CIS/ZnS-based WLED toward to warm light side, and the highest luminous efficacy is 42 lm/W. The results are summarized in table 1.

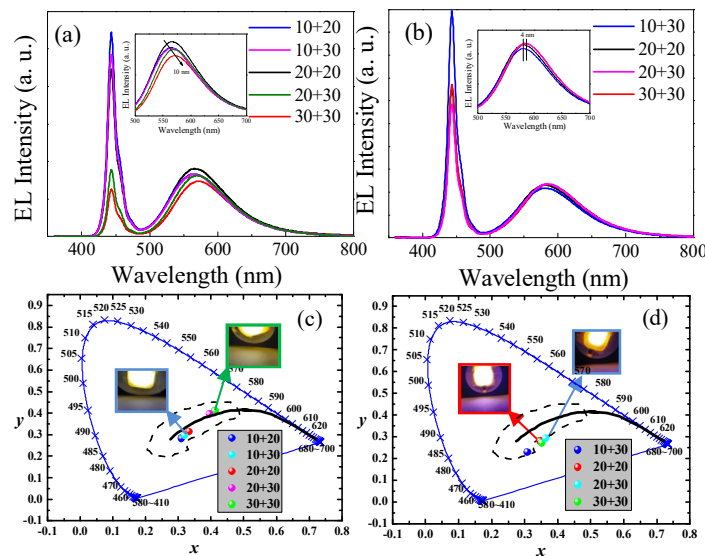


Figure 4. CIE coordinates of (a) CIS/ZnS and (b) CIS/ZnS:Al; Electroluminescence spectra of (c) CIS/ZnS and (d) CIS/ZnS:Al.

4. Conclusion

In this paper, CIS/ZnS and CIS/ZnS:Al core/shell QDs were synthesized by hot injection method. The emission wavelength, QY, and FWHM of CIS/ZnS QD is 533 nm, 84 %, and 74 nm, while that is 536 nm, 97 %, and 83 nm for CIS/ ZnS:Al QDs. The luminous efficacy and CRI of CIS/ZnS:Al WLED is 51 lm/W and 74, which is better than that of CIS/ZnS one. The Al doping is more effective to improve the QY, FWHM, and luminous efficacy. Therefore, the results show the evident to prove that the CIS/ZnS:Al QDs are quite suitable for SSL application.

Table 1. The performance of fluorescent film-based WLEDs.

Devices	QD content (wt%)	CRI	Efficacy (lm/W)	CCT (K)	CIE (x, y)
CIS/ZnS	10+10	0	40	0	(0.24, 0.18)
	10+20	67	39	7310	(0.31, 0.28)
	10+30	66	38	6380	(0.32, 0.30)
	20+20	64	42	5440	(0.33, 0.32)
	20+30	56	35	3770	(0.40, 0.40)
	30+30	55	32	3520	(0.41, 0.41)
CIS/ZnS:Al	10+10	0	44	0	(0.22, 0.12)
	10+20	0	50	0	(0.27, 0.19)
	10+30	71	49	10790	(0.31, 0.23)
	20+20	73	51	4460	(0.35, 0.28)
	20+30	70	50	3730	(0.36, 0.29)
	30+30	74	50	4020	(0.35, 0.27)

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