

Improving Stability of CIS/ZnS-Based White Light-Emitting Diodes by Silica Coating

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Abstract. Cadmium-free quantum dots (QDs) have been investigated for replacement cadmium-based QDs because of highly toxicity for humans and environmental such as CuInS₂/ZnS (CIS/ZnS) core/shell QDs that exhibit tunable emission wavelength and very broad emission spectrum. It often used in solid state lighting and white light-emitting diodes (WLEDs). This work reports on the synthesis of CIS/ZnS core/shell QDs using dodecanethiol (DDT) and zinc stearate as a precursor to form ZnS shell. Moreover, for improving the device stability, we coated SiO₂ on CIS/ZnS QDs surface. The crystal structure was analysis by transmission electron microscopy (TEM) and powder X-ray diffractometer (PXRD). The result shows that the emission wavelength of CIS/ZnS is 534 nm and with a high quantum yield (QY) of 107 %. The color rendering index (CRI), correlated color temperature (CCT) and luminous efficacy of SiO₂-coated WLED are 73, 4764 K, and 95 lmW⁻¹, respectively. Moreover, high stability of SiO₂-coated WLED can be obtained. The result indicates that CIS/ZnS@SiO₂ QDs have great potential to development of further WLED application.

1. Introduction

Semiconductor quantum dots (QDs) have widely attention in the field of solid-state lighting (SSL) [1], light emitting diodes (LEDs) [2-5], bioimaging [6] and solar cell [7] due to their appealing properties including excellent wavelength tunability, wide absorption and high quantum efficiency [8]. QDs are often made from II-VI systems, such as CdSe or ZnCdSe. However, Cd-based QDs are toxic for environment and humans, which limited for further industrialization [9, 10]. Non-toxic I-III-VI compounds have been replacement to Cd-based QDs such as ternary CuInS₂/ZnS (CIS/ZnS) core/shell QDs are investigated. For white light-emitting diodes (WLED), CIS/ZnS core/shell QDs have been intensively studied in several researches to improve quantum yields (QYs) and the luminescent properties, but the stability still low when fabricated on LED device. Recently, QDs-LED coated with SiO₂ have been developed to improving device stability and suppress energy transfer because of SiO₂ shell is highly transparent across wide range from infrared to visible zone [11, 12]. Here, we synthesized the CIS/ZnS QDs via a hot injection method with high QY 107% prepared SiO₂ shell coated on CIS/ZnS QDs surface by using 3-Aminopropyl-trimethoxysilane (APTES) and 3-Mercaptopropyl-trimethoxysilane (MPS) to improve the device stability.

2. Experimental

2.1. Materials

Copper (I) iodide (CuI, 99.99 %), 1-dodecanethiol (DDT, 98 %), 1-octadecene (ODE, 90 %), and zinc



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stearate ($\text{Zn}(\text{SA})_2$, 10-12 % Zn basis) were purchased from Aldrich. Indium acetate ($\text{In}(\text{AC})_3$, 99.99 %), (3-Mercaptopropyl) trimethoxysilane (MPS, 95 %), (3-Aminopropyl) triethoxysilane (APTES, 98 %) were purchased from Alfa Aesar. Toluene (99.5 %), hexane (99.7 %), acetone (99.9%), and methanol (99.7 %) were used as original without further purification.

2.2. Synthesis of $\text{CuInS}_2/\text{ZnS}$ core/shell QDs

$\text{CuInS}_2/\text{ZnS}$ (CIS/ZnS) QDs were synthesized by the hot injection method. Firstly, synthesized CIS core QDs. 0.0625 mmol of CuI, 0.5 mmol of $\text{In}(\text{AC})_3$ were added into 100 mL of three-necked flask and vacuum for 30 minutes, then added 5 mL of DDT with heated at 100 °C for 30 minutes, after that purged with argon and cool down at room temperature to form yellow solution. Consequently, heated above solution to 230 °C under heating rate of 15 °C/min. CIS QDs can be obtained after reacts for 5 minutes. Secondly, synthesized CIS/ZnS QDs. ZnS stock solution was prepared by mixing 8.3 mmol of $\text{Zn}(\text{SA})_2$, 1 mL of DDT, and 4 mL of ODE in three-necked flask and heated to 190 °C under argon atmosphere then reacted for 50 minutes. Finally, dropped ZnS solution into the CIS core solution at rate of 1mL/min. After that, heated to 240 °C and reacted for 120 minutes. The CIS/ZnS QDs was purified by excess methanol and collected precipitate, then purified by toluene/acetone/methanol (1:1:2) co-solvents and repeated this cycle for three times. The precipitates were dried at room temperature (RT).

2.3. Preparation of $\text{CIS}/\text{ZnS}@/\text{SiO}_2$ QDs

The CIS/ZnS QDs was coated with silica by mixing 0.07 g of QDs, 0.05 mL of MPS, 0.16 mL of APTES, and 40 mL of hexane. Those chemical were added in 250 mL of three-necked flask then heating to 65 °C with 8 °C/min of heating rate for 25 minutes. After that, cool down the solution to RT and purified with ethanol two times.

2.4. Fabrication of $\text{CIS}/\text{ZnS}@/\text{SiO}_2$ QDs-based WLEDs

The devices were fabricated in convert type by using 25 wt.% of QDs mixed with epoxy-based A: B gel, then dropped the mixtures into blue LED chip and cured its.

2.5. Characterization

The absorption spectrum of QDs were observed by using UV-Vis spectrophotometer (UV-vis, Hitachi UH5300). The emission wavelengths were observed by using fluorescence spectrophotometer (FL, Hitachi F-7000). The fluorescence QYs of QDs were calculated by integrating the FL area to compare with rhodamine 6G in ethanol solution. The crystal structure of QDs were measured by X-ray powder diffractometer (Bruker D8A25) with Cu $K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). The morphologies of QDs were observed by transmission electron microscope (TEM, JEOL JEM-2010).

3. Results and Discussion

3.1. Optical properties

The UV absorption and FL spectra of CIS/ZnS QDs are shows in figure 1 (a). We found that the emission wavelength of CIS/ZnS QDs is 534 nm and QY is 107 % with a full width at half maximum (FWHM) of 74 nm. Figure 1 (b) shows the FL spectra of CIS/ZnS@ SiO_2 QDs. We can find that the emission wavelength of CIS/ZnS shifts from 534 to 548 nm after SiO_2 coating.

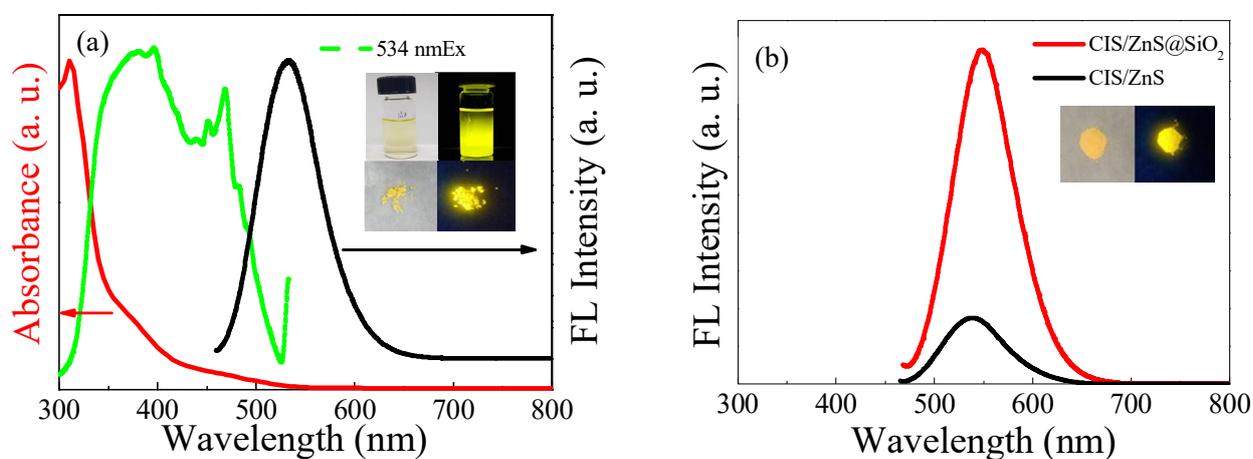


Figure 1. (a) UV and FL spectra of CIS/ZnS QDs.

(b) FL spectra of CIS/ZnS@SiO₂ QDs. compared with CIS/ZnS QDs.

3.2. Crystal structure and morphologies

The X-ray diffraction patterns of CIS, CIS/ZnS and CIS/ZnS@SiO₂ are presented in figure 2. By comparing the diffraction pattern of samples with JCPDS standard pattern of CIS and ZnS, we found that the diffraction peaks of CIS/ZnS QDs are 28.0°, 46.5° and 54.9°, respectively, which are corresponding to (112), (220), and (312) planes. It belongs to chalcopyrite phase. When coating with ZnS shell, the XRD peaks moved towards large angle, and close to zinc-blende phase, meaning that alloyed is formed. Figure 3 shows the TEM images of synthesized CIS/ZnS and CIS/ZnS@SiO₂ QDs. We found that the morphology of CIS/ZnS QDs are pyramid with average particle size 3.2 nm, the average size of QDs are increased to 3.5 nm after coating silica.

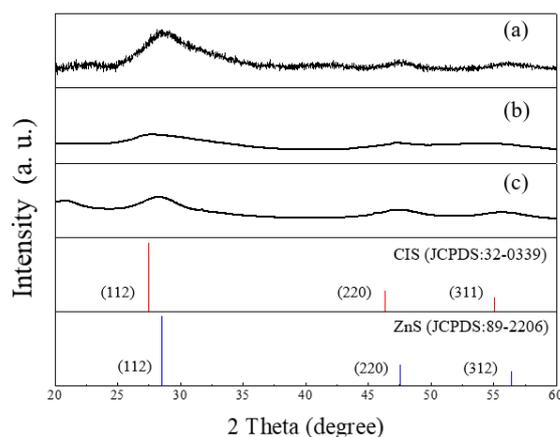


Figure 2. The XRD patterns of QDs. (a) CIS/ZnS@SiO₂, (b) CIS/ZnS, and (c) CIS core.

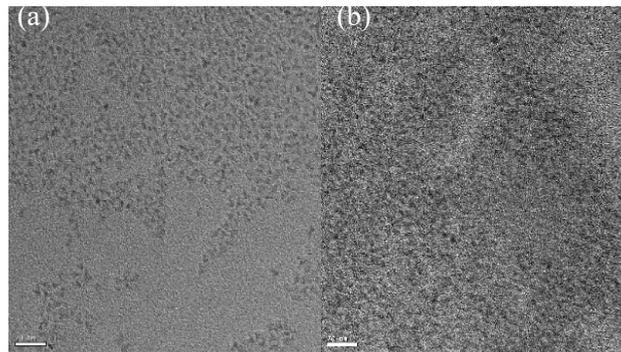


Figure 3. The TEM images of QDs. (a) CIS/ZnS and (b) CIS/ZnS@SiO₂.

3.3. Performance of WLEDs

For CIS/ZnS-based WLED, we found that it has CRI of 75, CCT of 6412 K, and luminous efficacy of 111 lmW⁻¹. The other hand, we can find that CRI of 73, CCT of 4764 K, and luminous efficacy decreasing to 95 lmW⁻¹ after coated with silica. The results are summarized in table 1. Compared the device stability between before and after coating with silica refer in figure 4, we found that the luminous efficacy of CIS/ZnS-based WLED decreased rapidly, while the luminous efficacy of CIS/ZnS@SiO₂-based WLED keep unchanged after working 8 h, meaning that the device has high stability.

Table 1. The CIE color coordinates, CCT, CRI and luminous efficacy of WLED with forward current 20 mA.

Devices	CIE (x, y)	CRI	CCT (K)	Efficacy (lm/W)
CIS/ZnS	(0.32, 0.26)	75	6412	111
CIS/ZnS@SiO ₂	(0.31, 0.26)	73	4764	95

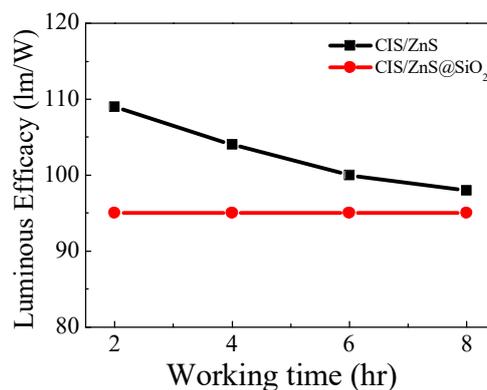


Figure 4. The luminous efficacy of QDs-WLED with forward current of 20 mA after working for 8 h.

4. Conclusion

In this study, the stability of CIS/ZnS core/shell QDs has been improved by coated with silica, and the CIS/ZnS@SiO₂ QD emitting yellow light at 548 nm, the crystal structure belongs to chalcopyrite phase and average particles size are 3.5 nm. The performance of CIS/ZnS@SiO₂-based WLED device have good improvement with high luminous efficacy value 95 lmW⁻¹, moderate CRI value of 73 and

CCT value of 4764 K with excellent device stability.

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