Encapsulate Materials Effect on ZnₙCd₁₋ₙS White Light Quantum Dots-Based White Light-Emitting Diodes

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Abstract. In this study, colloidal ternary ZnₙCd₁₋ₙS white light quantum dots (WQDs) were prepared, which have the characteristics of broad emission window. We used epoxy, styrene ethylene butylene styrene block copolymer (SEBS), and silicone as encapsulate materials to pack the device. The results show that the Zn₀.₅ and Zn₀.₈ have band edge and surface state emission. The quantum yield (QY) and particle size of Zn₀.₅ and Zn₀.₈ WQDs is 19, 32 % and 4.5±0.5 and 3.1±0.5 nm, respectively. The white light-emitting diodes (WLEDs) were obtained by mixing WQDs with different resins, and pumping by UV chip. The luminous efficacy is 6.7 and 8.5 lm/W for Zn₀.₅ and Zn₀.₈-based WLED by using epoxy resin as encapsulate material. Moreover, the long period test can maintain 201 and 184 h for Zn₀.₅ and Zn₀.₈-based WLED, respectively. The results of this study present that the device encapsulated by epoxy resin can improve the luminous efficacy and stability of device. This outstanding finding may contribute to the future development of solid-state lighting (SSL).

1. Introduction
Quantum dots (QDs) have high quantum yield (QY), wavelength tunability and broad excitation band [1], so they can be applied to many applications, such as solid state lighting (SSL) [2, 3] and display [4]. In order to improve the disadvantage of color rendering and self-absorption effects of commercially available white light emitting diodes (WLEDs) [5, 6], the white light quantum dots (WQDs)-based WLEDs were developed. The WQDs can cover the entire visible light range because of its broad emission window, and preparation of high color rendering WLEDs [7]. However, the low luminous efficacy and low stability of device limits the application in solid state lighting (SSL). The luminous efficacy and stability of WLEDs are affected by the transparency of the encapsulate materials. The compatibility between encapsulates and QDs is influence the performance of WLED. Chung et al. reported that the Zn₀.₅ and Zn₀.₈ WQDs were used silicone resin to pack WLED, the luminous efficacy of Zn₀.₅ and Zn₀.₈ are 1.0 and 4.1 lm/W [8], while used polyurethane Acrylic (PUA) UV resin to pack WLED, the luminous efficacy of Zn₀.₈ increases to 11.9 lm/W, and the long period test can maintain for 10 h [9]. In this study, three types of encapsulate materias are selected to form WLEDs, and the performances of WLEDs are compared.

2. Experimental

2.1. Chemicals
Cadmium oxide (CdO, 99.99 %) was purchased from Alfa Aesar. Stearic acid (SA, 99 %), zinc oxide (ZnO, 99.99 %), Sulfur (S, 99.99 %), 1-octadecene (ODE, 90 %), hexadecylamine (HDA, 90 %), and
trioctylphosphine oxide (TOPO, 90 %) were purchased from Sigma-Aldrich. Epoxy was purchased from Everwide Chemical Co., Ltd., SEBS block copolymer was purchased from Phon Tech Industrial Company, and silicone and UV chip provided by Lextar Electronics Corporation. The standard dye, rhodamine 101, used in quantum yield (QY) measurement, was also purchased from Aldrich. Hexane (99.7 %) and methanol (99 %) gotten from Macron Chemicals. All chemicals were used as received without purification.

2.2. Synthesis of Zn,Cd_{1-x}S quantum dots
0.15 mmol of CdO and 0.15 mmol of ZnO for Zn_{0.5}, 0.06 mmol of CdO and 0.24 mmol of ZnO for Zn_{0.8} and SA were placed in the three-necked flask and then heated to 230 °C under Ar flow. CdO, ZnO and SA powder was dissolved until the solution transfer to optical transparent with light yellow color. Meanwhile, the solution was cooled down to room temperature. HDA and TOPO were added into above solution and stirred together under Ar at room temperature, and then reheated up to 320 °C. S powder dissolved in ODE injected rapidly into the reaction flask and reacted at 290 °C to growth Zn_{0.5} and Zn_{0.8} QDs. After reacted for 60 min, the solution was cooled down to room temperature to stop the reaction. Samples were purified by adding methanol, and then dispersed in hexane for further measurement.

2.3. Preparation of white light-emitting diode
The Zn_{0.5} and Zn_{0.8} QDs blended with epoxy, SEBS, and silicone gel under different weight ratios, and then putted above mixture into 413 nm UV chip and cured at room temperature. The performance of WLEDs such as CIE coordinates, correlated color temperature (CCT, K), color rendering index (CRI) and luminous efficacy measured by integrating sphere. The samples were named as Zn_{0.5}-LED_{y,z} and Zn_{0.8}-LED_{y,z}. The y means the type of gel, and z means the weight percentage of QDs.

2.4. Characterization
The optical properties of samples measured with UV-vis spectrometer (UV-vis, Hitachi UH-5300 spectrometer) and fluorescence spectrophotometer (FL, Hitachi F-7000). Relative QY of samples was determined by comparing the peak area under the curve of FL emission for the Zn_{0.5} and Zn_{0.8} QDs with that of fluorescent dye (rhodamine 101 in ethanol). Transmission electron microscope (TEM, JEOL JEM-2010) was used to analyze the morphologies and size distribution of samples. The LED measuring system (ISUZU Optics, SLM-6Z) is used to measure the performance of devices.

3. Results and Discussion

3.1. FL spectra and TEM images of Zn,Cd_{1-x}S QD
The absorption and emission spectra of Zn_{0.5} and Zn_{0.8} QD shows in figure 1. We can find that the Zn_{0.5} and Zn_{0.8} QD have very broad emission window, which combines with band edge and surface state emission [8]. The band edge emission peak and QY of Zn_{0.5} and Zn_{0.8} QDs are 429, 409 nm, and 19, 32 %, respectively. Moreover, band edge emission is blue shift with increasing Zn content due to the larger band gap of ZnS. The photographs of Zn_{0.5} and Zn_{0.8} QD stored in the hexane under UV light is also shown in figure 1. The light color is warm and cold white light for Zn_{0.5} and Zn_{0.8} QD, respectively. This result is consistent with that reported by Siao and Chen et al. [8-11] In the TEM images we can find that the morphology of Zn_{0.5} and Zn_{0.8} is spherical with 4.5±0.5 and 3.1±0.5 nm
and the size distribution is uniform.

3.2. White light-emitting diodes

The Zn$_{0.5}$ and Zn$_{0.8}$ used as light conversion materials to form WLED. The EL spectra and CIE coordinates of WLED show in figure 2, and the light transmittance of encapsulates show in figure 3. We can find that the EL intensity of Zn$_x$-LED$_{epoxy}$ is higher than that of Zn$_x$-LED$_{SEBS}$ and Zn$_x$-LED$_{silicone}$ significantly, and the CIE coordinates close to the position of warm white light. We can find that the transmittance of epoxy and silicone film is higher than 80% in visible light range, while that of SEBS is lower 80%. The luminous efficacy of Zn$_{0.5}$-LED$_{epoxy}$, Zn$_{0.5}$-LED$_{SEBS}$, and Zn$_{0.5}$-LED$_{silicone}$ are 6.7, 5.2 and 5.9 lm/W, and that of for Zn$_{0.8}$-LED$_{epoxy}$, Zn$_{0.8}$-LED$_{SEBS}$, and Zn$_{0.8}$-LED$_{silicone}$ are 8.5, 5.6 and 8.0 lm/W, respectively. The results are summarized in table 1. The stability of Zn$_x$-LED$_{y,z}$ is shown in figure 4. The long period test of Zn$_{0.5}$-LED$_{epoxy}$, Zn$_{0.5}$-LED$_{SEBS}$, and Zn$_{0.5}$-LED$_{silicone}$ can maintain 201, 28 and 4 h, and the reliability for Zn$_{0.8}$-LED$_{epoxy}$, Zn$_{0.8}$-LED$_{SEBS}$, and Zn$_{0.8}$-LED$_{silicone}$ are 184, 161 and 44 h. We can find that the luminous efficacy and reliability of Zn$_x$-LED$_{epoxy}$ is better than that of Zn$_x$-LED$_{SEBS}$ and Zn$_x$-LED$_{silicone}$, owing to the light transmittance of the epoxy is the highest, and the compatibility with QDs is the best.

![Figure 1](image1.png)

**Figure 1.** (a) Absorption and emission spectra and (b) TEM image of samples. Insert photograph in (a) shows the Zn$_{0.5}$ and Zn$_{0.8}$ QDs under UV irradiation.

![Figure 2](image2.png)

**Figure 2.** The EL spectra (a) and CIE coordinates (b) of Zn$_x$-LED$_{y,z}$. Insert photographs show the devices under 20 mA injection current.
4. Conclusion

In conclusion, we present a facile thermal pyrolysis organometallic route to synthesize white light Zn$_x$ WQDs, and used epoxy, SEBS and silicone mixed WQDs to pack WLED. We can find that Zn$_{0.5}$ and Zn$_{0.8}$ QD have broad emission window, and QY is 19 and 32 %, respectively. The morphology of Zn$_{0.5}$ and Zn$_{0.8}$ QD is spherical. Using epoxy as encapsulate material, the Zn$_{0.8}$-LED$_{epoxy,33}$ device have the best luminous efficacy of 8.5 lm/W and operating time for 184 h. This study shows that the high light

![Figure 3. The transmittance of epoxy, SEBS, and silicone.](image)

Table 1. The properties of Zn$_x$-LED$_{y,z}$.

| QD     | gel   | CIE (x, y)   | CCT (K) | CRI | Efficacy (lm/W) |
|--------|-------|--------------|---------|-----|-----------------|
| Zn$_{0.5}$ | epoxy | (0.43, 0.36) | 2760    | 85  | 6.7             |
|        | SEBS  | (0.41, 0.38) | 3775    | 86  | 5.2             |
|        | silicone | (0.40, 0.38)| 4508    | 90  | 5.9             |
| Zn$_{0.8}$ | epoxy | (0.40, 0.35) | 3379    | 83  | 8.5             |
|        | SEBS  | (0.41, 0.38) | 3392    | 83  | 5.6             |
|        | silicone | (0.40, 0.38)| 3593    | 83  | 8.0             |

![Figure 4. Stability of Zn$_x$-LED$_{y,z}$ for long period of working time under 20 mA.](image)

Insert diagram shows the CRI variation of devices.

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transmittance of the encapsulate material and the good compatibility of the QDs enhance the luminescent properties of the WLED.

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