Inorganic InP/ZnS Quantum Dots: Optical Properties and Fabrication in Display Application

Chaikit Chumchujan¹, Shu-Ru Chung¹

¹Department of Materials Science and Engineering, National Formosa University, Yunlin 63201, Taiwan
srchung@nfu.edu.tw

Abstract. Inorganic InP/ZnS quantum dots (QDs) is one kind of optoelectronic materials owing to the high quantum yield (QY) and non-toxicity. In this study, green light InP/ZnS QDs with high QY were synthesized by one-pot injection method and mixed with red light CsPbBrI₂ QDs as converting material. Those converting material blend with epoxy glue, and pumping by InGaN blue chip to form white light-emitting diode (WLED). The results show that the CIE of WLED provides at (0.31, 0.33) with NTSC of 90%.

1. Introduction
In the past, fluorescent backlight is used and play an important role in display application. However, there are huge drawbacks [1, 2]. Firstly, it is high energy consumption due to high turn on voltage. Secondary, the color gamut of fluorescent lamp backlight is low, as 70 % of NTSC [3, 4]. Thus, it is replaced with WLED-based backlight. WLED-based backlight in displays are normally combined with blue LED and phosphors [5]. Choosing Cd-based quantum dots (QDs) as the phosphors due to QDs have a narrow full width at half maximum (FWHM), resulting in increasing the color gamut [6]. However, Cd-based has some disadvantages. It is high toxicity. Moreover, it has low PL quantum yield (QY) because of self-quenching [7]. Thus, InP nanoparticles are good choices because of they are non-toxicity, while the luminescence efficiency in near IR spectral range with very low QY due to easy to oxide [8]. Therefore, coating with a high band gap material such as ZnS and ZnSe on the InP surface to form InP/ZnS core/shell structure is necessary. It leads to increasing the QY and energy band gap of QDs. From the literature review, it provides the result that the QY of InP/ZnS QDs is between 30-60 % [9]. It depends on the molar ratios between myristic acid and indium, reaction temperature, as well as reaction time. The best condition in InP/ZnS synthesis is that the molar ratio of myristic acid: indium is 3.5:1 and the reaction time is 3-5 hours. Furthermore, increasing of reaction temperature also make increase QY [10].

2. Experimental methods

2.1. Chemicals
Zinc (II) iodide (ZnI₂, > 98 %) and indium (III) chloride (InCl₃, 99.995 %) were purchased from Acros Organics. Zinc (II) bromide (ZnBr₂, 98 %), Myristic acid (MA, 98 %) and Hexamethylphosphorous triamide (HMPT, 97 %) were purchased from Alfa Aesar. 1-dodecanethiol (DDT, > 98 %) 1-octadecene (ODE, 90 %) and oleylamine (OLA, 70 %) were provided by Aldrich.

2.2. Synthesis of green InP/ZnS QDs
In synthesis green InP/ZnS QDs, 0.72 mmol of InCl₃, 0.72 mmol of MA, and 2.16 mmol of Zn precursors (ZnI₂: ZnBr₂ = 1:1) were purged by Ar gas for 10 minutes, and then they were mixed with 10 mL OLA and ODE (the ratio of OLA: ODE was 6:4) in three-necked round-bottom flask. The mixture was stirred and degassed at 110 °C for 45 minutes followed by rapidly heated to 220 °C under Ar atmosphere. Next, 0.2 mL of HMPT was quickly injected above mixture and controlled temperature at 220 °C for 15 minutes, after that quickly quenched to 200 °C, then 3 mL of DDT was slowly injected and maintained the temperature at 200 °C for 6 hours. InP/ZnS QDs were precipitated with an excess of ethanol and purified with ethanol by centrifuge. Finally, purified InP/ZnS QDs were re-dispersed in hexane for characterization.

2.3. Fabrication of White Light-Emitting Devices
InP/ZnS QDs were blended with CsPbBrI₂ QDs and re-dispersed with hexane, then hexane was repelled in vacuum desiccator. The mixture of QDs were mixed in epoxy-based AB glue. The ratio of A: B glue was 1:2. Next, the mixture was stirred to be homogenous. Finally, it was put on 3020 InGaN blue chip and the device performance was measured by integrated sphere (Isuzu Optical, ISM-360) at a driving current of 20 mA.

2.4. Materials characterization
Purified InP/ZnS QDs were dispersed in hexane for optical properties. They were measured by fluorescence spectrophotometer (FL, Hitachi F-7000) and ultraviolet-visible spectrometer (UV-Vis, Hitachi UH5300). PLQY of the QDs was calculated by comparing the FL emission area of QDs, which were dispersed in hexane, with Rhodamine 6G in methanol as a reference sample at wavelength 450 nm. The morphology and size distribution of QDs were observed by transmission electron microscopy (TEM).

3. Results and discussion

3.1. Optical properties of InP/ZnS QDs
Figure 1 shows the absorption, excitation and emission spectra of the synthesized InP/ZnS QDs. It displays that the emission wavelength of sample is 500 nm with nonobvious absorption edge. The PLQY of green QDs were measured to be 113 % with FWHM of 70 nm.
3.2, Morphologies of InP/ZnS QDs
The TEM images of sample are presented in figure 2. It can be found that it has good dispersion and the morphologies are spherical shape. The particle size ranges from 2.6 to 3.0 nm.

3.3, InP/ZnS QDs-based WLED
InP/ZnS QDs were mixed with CsPbBrI$_2$ and then this mixture was mixed with AB glue. The ratio of green light InP/ZnS QDs: red light CsPbBrI$_2$: AB glue is 0.503 g:0.006 g:1.000 g. Above mixture is putted on the blue LED and can produce white light under 20 mA current. The Commission International d’Eclairage (CIE) chromaticity coordinates shows in figure 3 (a) and EL spectra of device shows in figure 3 (b). It can be seen that the CIE chromaticity coordinates locates at (0.31, 0.34). Moreover, the luminous efficacy, CCT, and CRI of WLED are 11 lm/W, 6523 K, and 88, respectively. After filters the white light by color filter and calculate, the color gamut of WLED is 90 % of NTSC, as shown in figure 4.

4. Conclusion
In this paper, the green InP/ZnS QDs were successfully prepared with one pot injection method. The QY and particle size of InP/ZnS QD are 113 % and 2.6-3.0 nm. For the WLED performance, we can
get the CIE color coordinates (0.31, 0.33) and 90% of NTSC after blending with red light CsPbBrI₂ QD.

**Acknowledgment**
This work was supported by the Ministry of Science and Technology of Taiwan under Contract nos. 107-2221-E-150-034 and 108-2221-E-150-016.

**References**
[1] Yin L., Bai Y., Zhou J., Cao J., Sun X. W., Zhang J. H. 2015 The thermal stability performances of the color rendering index of white light emitting diodes with the red quantum dots encapsulation *Opt Mater* **42** 187-92.
[2] Yoshinori S., Kensho S., Yasunobu N. 1999 Light emitting device and display *US Patent* **5** 998, 925.
[3] Yang H. Lee D. K., Kim Y. S., 2009 Spectral variations of nano-sized Y₃Al₅O₁₂:Ce phosphors via codoping/substitution and their white LEDs characteristics *Mater. Chem. Phys.* **114** 665-9.
[4] Ito Y., Hori T., Kusunoki T., Nomura H., Kondo H. 2014 A phosphor sheet and backlight system providing wider color gamut for LEDs *J. Soc. Inf. Disp.* **22** 419-28.
[5] Wu Y., Wanlu Z., Guilin Z., Jiatao Z., Guoxing H., Ruiqian G. 2018 Super-high color temperature tunable white LEDs based on high quality InP/ZnS quantum dots via myristic acid passivation and Ag doping *Opt Com* **418** 46-50.
[6] Wu Y., Guoxing H., Shiliang M., Jiatao Z., Qiuhang C., Guilin Z., Ruiqian G. 2017 Controllable synthesis of dual emission Ag:InP/ZnS quantum dots with high fluorescence quantum yield *App Sur Sci* **423** 686-94.
[7] Han Z., Ning H., Zaiping Z., Qinli L., Fengjuan Z., Aiwei T., Yu J., Linsong L., Huaibin S., Feng T., Zuiliang D. 2019 High-Efficiency Green InP Quantum Dots-Based Electroluminescent Device Comprising Thick-Shell Quantum Dots *Adv. Optical Mater.* **7** 1801602.
[8] F. Angel-Huerta, M.P. Gonzalez-Araoz, J.F. Sanchez-Ramirez, J. Diaz-Reyes, J.L. Herrera-Perez, J.S. Arias-Ceron. J.G. Mendoza-ALvarez 2018 Synthesis temperature-dependent optical properties of ZnS-shell formation on InP nanoparticles *Jou of Lum* **197** 277-84.
[9] Feng Z., Jicun R. 2012 Gas-liquid phase synthesis of highly luminescent InP/ZnS core/shell quantum dots using zinc phosphide as a new phosphorus source *J. Mater Chem.* **22** 1794-9.
[10] Liang L., Peter R. 2008 One-pot synthesis of Highly Luminescent InP/ZnS Nanocrystals without Precursor Injection *JACS Com.* **130** 11588-9.