Synthesis of highly efficient ZnAgInS-ZnInS/ZnS quantum dots and application for down-converted LEDs

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ABSTRACT

This study introduces innovative exothermic reaction assisted synthetic method for highly efficient green emitting ZnAgInS-ZnInS/ZnS quantum dots (QDs) by simply adding excess amounts of Zn precursors (Zinc acetate dehydrate, ZAD) and application for down-converted light emitting diodes (LEDs). The ZnAgInS-ZnInS/ZnS QDs were synthesized using multi-step hot-injection method: Ag-In-S core growth, Zn-Ag-In-S core-alloy, Zn-In-S inner-shell, Zn-S outer-shelling. We compared low and high concentration of ZAD in order to make different reaction conditions during formation of ZnAgInS-ZnInS/ZnS QDs. We found when we use high concentration of ZAD, ZnInS inner-shell was successfully synthesized between ZnAgInS core-alloy and ZnS shell and photoluminescence quantum yield (PLQY) of QDs was increased by the exothermic reaction. The PLQY of QDs using high concentration of ZAD (86%) shows 1.43 times higher than that of QDs using low concentration of ZAD (60%) [1]. Dominant wavelength of QDs using high concentration of ZAD (511 nm) show blue shift about 15 nm compared to QDs using low concentration of ZAD (536 nm). Finally, we realized tri-packaged white LEDs using ZAIS green emitting QDs, ZCIS red emitting QDs and 445 nm blue emitting LED. The tri-package white LEDs show the luminous efficacy (LE) of 72 ~ 98 lm/W, color rendering index of 88 ~ 94 and high TM-30-2015 values from 2700 K to 10000 K of correlated color temperature (CCT). The highly efficient, broad band emitting ZnAgInS-ZnInS/ZnS QDs can be a good candidate for color converting materials in the field of LED lightings.

Keywords: quantum dots, multi-step hot injection method, exothermic reaction, color quality, and down-converted LED

1 INTRODCTION

Cd-free III-V and I-III-VI based quantum dots (QDs) are an attractive color converting materials for application of displays and lightings [2-4]. III-V based QDs, such as InP, are developed for display backlight due to the narrow full width at half maximum (FWHM) [5, 6]. For this reason, the QDs hardly adopted for lighting applications because the color qualities of lightings cannot be improved with narrow FWHM. In this study, we synthesize the broad band emitting I-III-VI based QDs, such as AgInS and CuInS QDs, due to donor-acceptor pair (DAP) recombination [7-9] and fabricate down-converted LEDs for high color quality white lighting application.

First, we synthesized highly efficient broad band emitting green ZnAgInS-ZnInS/ZnS (ZAIS) alloy core-inner shell/outer shell QDs with exothermic reaction assisted multi-step hot-injection method by adding excess amount of zinc precursor (zinc acetate dehydrate, ZAD) at the shelling step. The strong exothermic reaction during alloying-shelling process helps formation of ZnInS inner shell and surface passivation [1, 9, 10]. The broad band emitting red CuInS/ZnS (ZCIS) QDs were synthesized and characterized in our previous study [1, 10].

Second, we fabricate the down-converted LEDs to realize high color quality white LEDs and measured their optical properties such as luminous efficacy (LE), color rendering index (CRI, R_a), TM-30-2015 (color fidelity index (R_f), color gamut score (R_g) and color icon) to evaluate the color qualities for lighting application. The two-measure system TM-30-2015 was developed to solve the problems of overestimation of high-CRI values from Illuminating Engineering Society of North America (IES) [11-13].

2 EXPERIMENTAL

2.1 Synthesis of ZAIS QDs [1]

To synthesize the ZAIS QDs, $AgNO_3$, $In(acac)_3$, OA, and ODE (core precursors) were loaded in a three-neck flask and purged in a N_2 atmosphere for 20 min at room temperature. Then, OTT was injected in to the three-neck flask at 90 ^oC and reacted for 30 min. After then, for growth of core, the core precursors were heated to 120 ^oC and S and OLA mixture was injected into the reaction solution and reacted for 3 min. After core growth, the first and second alloying-shelling processes were conducted by adding high and low concentration of ZAD, OA and OTT solution and heated to 180 ^oC for 2 hours and 230 ^oC for 2 hours, respectively. Final two step outer-shelling processes were conducted by injecting the shelling precursors at 180 ^oC for 2 hours. We synthesized ZnAgInS-ZnInS/ZnS alloy core-inner shell/outer shell QDs by injection of high concentration of ZAD, and ZnAgInS/ZnS core/shell QDs by injection of low concentration of ZAD. The synthesized ZAIS QDs were purified by centrifugation and dissolved in hexane.

2.2 Fabrication of down-converted LEDs

To realize down-converted LEDs with ZAIS and ZCIS QDs, the QD solution were mixed with silicon binder and dried at 70 ^{o}C to evaporate the solvent. After then, the dried mixture was put in to an InGaN blue LED packages and hardened. As previously reported, the green and red emitting down-converted LEDs were realized using long-wavelength pass dichroic filters (LPDFs) [1, 14].

2.3 Characterization

The photoluminescence of ZAIS QDs were measured using a Xe lamp and spectrometer (Darsa, PSI Trading. Co., Ltd) and the photoluminescence quantum yield (PLQY) was calculated by comparing with rhodamin 6G (PLQY of 95% in ethanol and optical density of 0.05 at 450 nm). The electroluminescence (EL) of down-converted LEDs was measured using a spectrometer (Darsapro-5000, PSI Trading Co., Ltd.) in an integrated sphere with applied current of 60 mA for single package LED and 180 mA for tri-package LEDs.

3 RESULTS AND DISCUSSION

Figure 1 shows the PL spectra and 1931 CIE color coordinates of synthesized ZnAgInS-ZnInS/ZnS QDs with high concentration of ZAD and ZnAgInS/ZnS QDs with low concentration of ZAD. All QDs show broad band emission around 90 nm of FWHM due to the DAP recombination in the core QDs. The AgInS core shows amber color with the emission peak around 586 nm ~ 590 nm. After final two step of outer shelling process, the emission peak of ZnAgInS-ZnInS/ZnS alloy core-inner shell/outer shell QDs were shifted from 586 nm to 511 nm and ZnAgInS/ZnS core/shell QDs were shifted from 590 nm to 533 nm. The emission wavelength of QDs tend to blue shift during shelling processes because of band engineering of core/inner shell/outer shell or core/shell and core etching. The PLQY of ZnAgInS-ZnInS/ZnS alloy core-inner shell/outer shell QDs using high concentration of ZAD show dramatically enhanced up to 86% by reducing the surface defects and formation and band engineering of ZAIS inner shell during exothermic reactions. The PLQY of ZnAgInS-ZnInS/ZnS QDs shows 1.43 times higher than that of ZnAgInS/ZnS QDs, using low concentration of ZAD (60%). We previously reported the structural and optical properties of these two types of QDs with various measurements of X-ray diffraction patterns, X-ray photoelectron spectroscopy analysis, raman spectroscopy, and transmission electron microscopy [1]. As shown in Figure 1, the synthesized ZAIS QDs show broad band emitting FWHM around 90 nm. This means that the ZAIS QDs as well as ZCIS QDs can be good candidates for high color quality white LED lighting application. Therefore, to check the optical properties of QD down-converted LEDs, we fabricated down-converted LEDs using broad band emitting green ZAIS QDs, red ZCIS QDs and 445 nm blue emitting LEDs [1]. The down-converted LEDs were easily fabricated by put silicon and QD mixture into blue LED package.

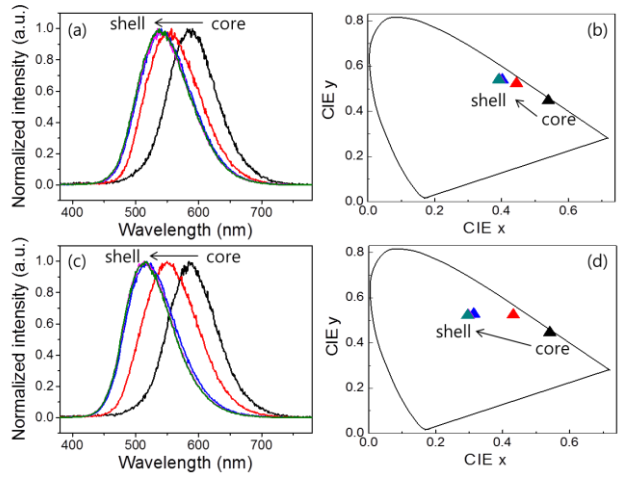

Figure 1: (a) PL spectra and (b) 1931 CIE color coordinates of ZnAgInS/ZnS QDs (synthesized with LZAD). (c) PL spectra and (d) 1931 CIE color coordinates of ZnAgInS-ZnInS/ZnS QDs (snthezied with HZAD).

	LZAD	HZAD
LE (lm/W)	112	137
CCT (K)	4115	6693
CRI (R_a)	63	60
R_f	62	64
R_g	86	78

Table 1: The optical properties of ZIAS QDs down-converted LEDs synthesized using LZAD and HZAD.

Figure 2 shows EL spectra, 1931 CIE color coordinates, and luminous efficacy of QD down-converted LEDs. The green emitting from ZAIS QDs slightly shifted toward reddish color due to aggregation and reabsorption of QDs in high concentration of QDs of down-converted LED package. The luminous efficacy of down converted LEDs using ZnAgInS-ZnInS/ZnS alloy core-inner shell/outer shell QDs shows 1.22 times higher than that of down converted LEDs using ZnAgInS/ZnS core/shell QDs. The down converted LED using ZnAgInS-ZnInS/ZnS alloy core-inner shell/outer shell QDs with the silicon binder and QD solution mixture loading amount of 1.0 ml shows the maximum luminous efficacy of 137 lm/W with the 1931 CIE color coordinates of (0.299, 0.392) at the rated current of 60 mA.

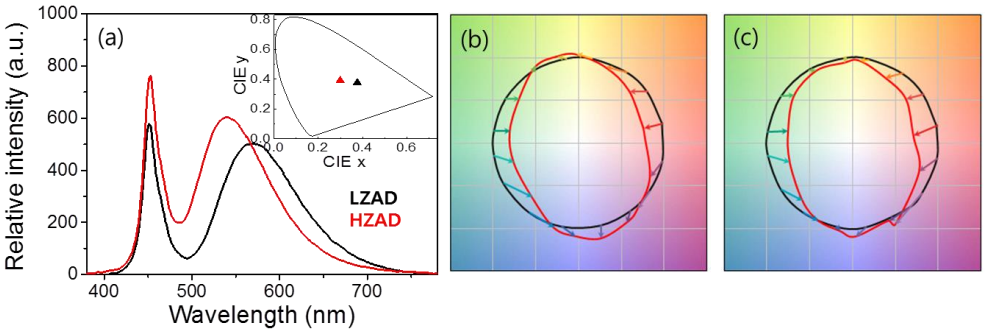

Figure 2: (a) EL spectra (inset: 1931 CIE color coordinates) of down-converted LEDs using ZAIS QD with LZAD (black) and HZAD (red). The color icon of down-converted LED with (b) LZAD and (c) HZAD. (Reference source: black circle, sample source: red circle)

However, As shown in Figure 2 and Table 1, the color qualities of the down-converted LEDs using only green QDs show very low values and color icons have many distortion of colors compared to the reference light source.

To enhance the color quality of white LEDs, we introduce the tri-package white LEDs combined with ZAIS green and ZCIS red down-converted and LPDF-capped LEDs and InGaN blue LED (See EL spectra in Figure 3(a)). By changing the applied current of each colored LED, the CCT of white LEDs can be easily changed from 2700 K (warm white) to 10000 K (cool white). Figure 3 and Table 2 show the optical properties of tri-package white LEDs. Figures 3(b) and 3(c) shows EL spectra and 1931 CIE color coordinates of white emission with various CCTs from 2700 K (warm white) to 10000 K (cool white). The blue and green emissions were increased and red emission was decreased by changing the CCT from warm to cool white.

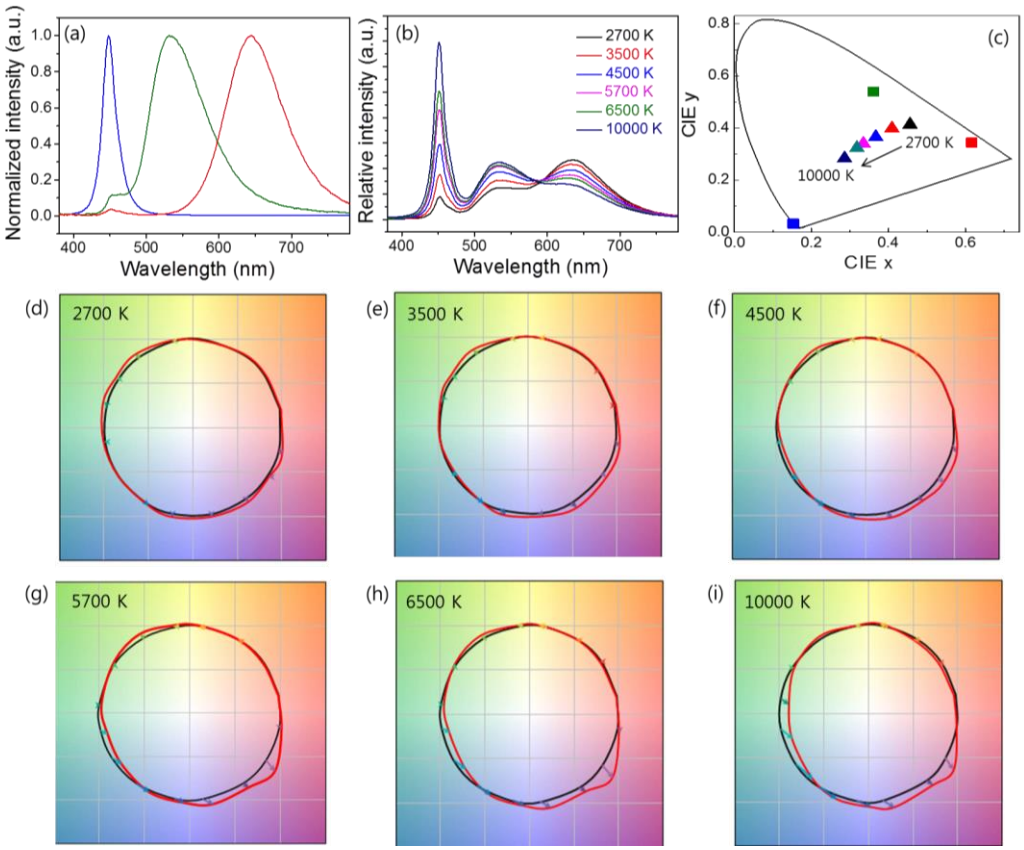

Figure 3: (a) EL spectra of ZAIS green and ZCIS red down-converted LEDs and blue LED. (b) EL spectra and (c) 1931 color coordinates of tri-package white LEDs from the CCT of 2700 K to 10000 K. The color icons of tri-package white LEDs with various CCTs (d) 2700 K, (e) 3500 K, (f) 4500 K, (g) 5700 K, (h) 6500 K, and (i) 10000 K. (Reference source: black circle, sample source: red circle)

CCT (K)	2758	3407	4393	5575	6418	9745
LE (lm/W)	72	81	90	96	96	98
CRI (R_a)	94	94	93	91	90	88
R_f	94	91	89	86	84	81
R_g	104	105	104	104	103	101

Table 2: The optical properties of tri-package white LEDs combined with blue LED, green ZIAS QDs and red CIS QDs down-converted LEDs.

The optical properties of the tri-package white LEDs show good luminous efficacy and high color qualities almost all range of CCTs. The LE of tri-package white LEDs shows low value in the warm white because the ZCIS red down-converted LED has low LE (~46 lm/W) compared to ZAIS green down-converted LED (~160 lm/W). However, the color qualities such as CRI, R_f and R_g show excellent values in the warm white CCTs. Figures 3(d) ~ 3(i) show the color icon of tri-package white LEDs with various CCTs. The color icon of warm white (Figures 3(d) ~ 3(f)) with the CCT range of 2700 K ~ 4500 K, show excellent color matching between the reference source and sample source.

4 CONCLUSION

The highly efficient green emitting ZnAgInS-ZnInS/ZnS alloy core-inner shell/outer shell QDs were successfully synthesized with exothermic reaction assisted multi-step hot-injection method by adding excess amount of ZAD at the shelling step. The strong exothermic reaction during alloying-shelling process helps formation of ZnInS inner shell and surface passivation.

Also, we fabricate the high color quality tri-package white LEDs using broad band emitting green ZAIS and red ZCIS QDs and blue LED. The LEs of white LEDs have 72 ~ 98 lm/W and CRI show 88~ 94 at the CCT of 2700 K ~ 10000 K. The TM-30-2015 (R_f, R_g and color icon) show excellent values (81~94 for R_f and 101 ~ 104 for R_g) and well matched color icon between reference and sample source. The results mean that the ZAIS and ZCIS QD down-converted LEDs can be a good candidate for excellent color quality of white LED lighting application with a good luminous efficacy and simple fabrication method.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP (Ministry of Science and ICT&Future planning)) (No. 2016R1A5A1012966 and No. 2016R1A6A3A11932485).

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