Enhancing the Color Rendering Index for Phosphor-converted White LEDs Using Cadmium-Free CuInS\textsubscript{2}/ZnS QDs

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Culn\textsubscript{2} (CIS) I–III–VI-type quantum dots (QDs) were synthesized under different growth times by the facile solvothermal method. Emission wavelengths showed a deep red region (630 - 650 nm) with low quantum yields (QYs). The core CIS was effectively passivated by the coating layer of ZnS, thereby remarkably increasing the QYs (48% and 82%) and causing the blue shift of the emission band (580 - 623 nm). Red-emitting CIS/ZnS QDs that were blended with Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}:Ce\textsuperscript{3+} phosphor-based white light-emitting diodes (LEDs) were further demonstrated. The color rendering index of white LEDs was improved \((R_a = 86)\) by using red-emitting CIS/ZnS QDs with broader spectra. The optical properties were evaluated under various forward currents; these properties included the electroluminescence spectra and luminous efficiency of CIS/ZnS QDs-assisted white LEDs. These results clearly showed that CIS/ZnS QDs are promising candidates for application in white LEDs.

Keywords: CuIn\textsubscript{2} I–II–VI; Quantum dots; White light-emitting diodes; Color rendering index.

INTRODUCTION

Solid-state white light-emitting diodes (LEDs) have rapidly become promising alternative illumination sources because of their low power consumption, high luminous efficiency, and long lifespan.\textsuperscript{1} The most common commercial white LEDs to date have been fabricated on blue InGaN LED chips with yellow-emitting Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}:Ce\textsuperscript{3+} (YAG:Ce) phosphors because of their simpler processing and more cost-effective assembly. The blue light from the blue chips are mixed with the yellow-emitting YAG:Ce phosphors, thereby producing white light. In addition, yellow-emitting YAG:Ce phosphors have stable colors because of the stable thermal ability of their structures.\textsuperscript{1,2} However, commercial white LEDs lack the red spectrum. A high color rendering index (CRI; also known as \(R_j\)) value that is greater than 80 is difficult to achieve. To improve the low CRI values, red phosphors can be used in white LEDs. However, the use of red phosphors presents some problems. For instance, sulfide red phosphors are chemically unstable,\textsuperscript{3,4} whereas the synthesis of nitride phosphors requires high nitrogen pressure and high temperatures.\textsuperscript{5–7}

Red-emitting semiconductor quantum dots (QDs) such as CdSe with high photoluminescence (PL) quantum yields (QYs) have shown potential for incorporation into white LEDs.\textsuperscript{8,9} Their optical properties can be tuned to specific sizes and shapes because of quantum-confinement effects.\textsuperscript{10,11} This property is particularly attractive as compared with traditional phosphors.\textsuperscript{12,13} Unfortunately, the toxicity of CdSe has limited its application. Preventing the release of the heavy metals by CdSe is difficult even after passivation by a ZnS shell. In the last two decades, research has shifted toward the synthesis of non-toxic III–V-type\textsuperscript{14} and I–III–VI–type\textsuperscript{15} QDs. Ternary I–III–VI-type QDs such as Culn\textsubscript{2} (CIS),\textsuperscript{16–18} AgIn\textsubscript{S},\textsuperscript{19,20} and CuGa\textsubscript{2}\textsuperscript{21} have been synthesized and characterized because they exhibit high absorption and emission. Meanwhile, non-toxic InP/ZnS-based white QD-LEDs have been fabricated and reported to have a CRI value of 86.\textsuperscript{22} For general lighting application, I–III–VI-type CIS QDs exhibit a relatively broad emission bandwidth (typically > 100 nm) as compared with the II–VI-type CdSe and III–V-type InP QDs because the radiative recombination process of CIS QDs is accompanied by defect-related intra-gap states.\textsuperscript{23}

In this work, non-toxic CIS QDs and CIS/ZnS QDs were synthesized by the facile solvothermal method, and their luminescent properties were investigated. Red-emitting CIS/ZnS QDs and yellow-emitting YAG:Ce phosphor were coated onto an InGaN blue chip (\(\lambda_c = 460 \text{ nm}\)), and the optical properties of the white LEDs were evaluated. The white LEDs with red-emitting CIS/ZnS QDs-assisted
YAG:Ce phosphors exhibited improved CRI values with $R_a = 86$, thereby suggesting that these white LEDs are potential candidate light sources.

**EXPERIMENTAL SECTION**

**Materials.** Copper(I) iodide (CuI; 99.99%), 1-dodecanethiol (DDT; 98%), and 1-octadecene (ODE; 90%) were purchased from Sigma–Aldrich. Indium acetate (In(Ac)$_3$; 99.99%) was purchased from Alfa Aesar. Zinc stearate (10%-12% Zn basis) was purchased from J. T. Baker.

**Synthesis of CuInS$_2$ Cores and CuInS$_2$/ZnS Core/Shell QDs.** The CuInS$_2$ (CIS) core QDs were synthesized by solvothermal method. CuI (0.25 mmol), In(Ac)$_3$ (1.0 mmol), and DDT (15.0 mL) were used as starting materials, which were mixed in a Teflon-lined autoclave. In this process, DDT was used as both the solvent and the sulfur source. The autoclave was sealed and heated at 180 °C for 8 h. After cooling to room temperature, the dark red crude solution of CIS core QDs was obtained. To coat the surface of the CIS core QDs with ZnS, the ZnS stock solution of Zn stearate (8 mmol), DDT (2 mL), and ODE (8 mL) was mixed with approximately 15 mL of the CIS QD crude solution and heated at 200 °C for 14 h. The resulting CIS and CIS/ZnS QDs were isolated and purified several times by adding ethanol/chloroform. The CIS and CIS/ZnS QDs were then collected by centrifugation (7000 rpm, 10 min). The final precipitate was dispersed in chloroform.

**Fabrication of CIS/ZnS QD-assisted YAG:Ce phosphor-based white LEDs.** First, 0.28 g of thermally curable silicone resin (OE-6630 B, Dow Corning Co.) was blended with the red-emitting CIS/ZnS QDs that were dispersed in chloroform. The chloroform in the mixture was then evaporated by heating at 70 °C for 1 h. Second, the gelatinous red-emitting CIS/ZnS QDs were prepared by adding an equal amount (0.28 g) of the hardener (OE-6630 A) to the mixture of red-emitting CIS/ZnS QDs and silicone resin. Inorganic yellow-emitting YAG:Ce phosphor particles were added to the mixture. The weight percentages of the phosphors and QDs in the epoxy resin were 12 wt % and 20 wt %, respectively. Finally, the silicone resin mixture containing the yellow-emitting YAG:Ce phosphor and the red-emitting CIS/ZnS QDs was dispensed onto the surface of a blue LED chip (InGaN). The chip was heated in a two-step thermal curing process at 80 °C for 2 h and then at 150 °C for 1 h in an oven.

**Characterization.** The UV/Vis absorption spectra of the colloidal semiconductor nanocrystals of CuInS$_2$ (CIS) and CIS/ZnS QDs were obtained at room temperature using a Shimadzu UV-700 spectrophotometer with a 1 cm wide quartz cell at room temperature. PL spectra were collected using a FluoroMax-3 spectrophotometer equipped with a 150 W Xe lamp and a Hamamatsu R928 photo-multiplier tube. The nanoparticles were analyzed by X-ray diffraction (XRD) using a Bruker D2 Phaser diffractometer that was operated in transmission mode with Cu-K$_\alpha$ radiation ($\lambda = 1.5418$ Å). The data were collected over a 20 range from 20° to 70° at intervals of 0.02°, with a counting time of 30 s per step. PL quantum yields (QYs) of the CIS and CIS/ZnS QDs dispersed in chloroform were calculated by comparing their integrated emissions with that of rhodamine 6G (QYs of 96%) in an ethanol solution. The electroluminescent (EL) spectrum, luminous efficiency, correlated color temperature, Commission Internationale de l’Eclairage (CIE) color coordinates, and CRI of the as-fabricated QD–LEDs were measured under various forward currents, ranging from 20 mA to 120 mA in an integrating sphere with a diode array rapid analyzer system (Everfine Photo–E-Info Co. Ltd.).

**RESULTS AND DISCUSSION**

The absorption spectra of CuInS$_2$ (CIS) QDs with solvothermal growth times of 6 and 8 h are shown in Fig. 1(a). The QDs grown for 8 h had longer wavelength absorption than those grown at 6 h, because of the reduced
quantum confinement effect in QDs. The absorption bands of the CIS/ZnS core/shell were shifted to a shorter wavelength after ZnS coated the CIS QDs, thereby causing a blue shift in their absorption spectra, as shown in Fig. 1(b). The band gap extension of CIS/ZnS core/shell has been investigated in the literature. This effect was probably due to the surface etching of the core CIS QDs or the generation of alloyed interfacial CIS/ZnS when ZnS was added. Subsequently, the effective core of CIS QDs was reduced. Both CIS QDs exhibited red emissions at 650 nm and 680 nm with broad bandwidths of 115 nm and 118 nm, respectively. The quantum yields (QYs) of the 6 h and 8 h CIS QDs that were calculated with an excitation wavelength of 450 nm were 1.2% and 3.4%, respectively. In addition, the emission spectra of the CIS(6 h)/ZnS and CIS(8 h)/ZnS were shifted to the blue wavelengths and peaked at 580 nm and 623 nm, respectively, as shown in Figs. 2(a) and 2(b). The QYs of CIS(6 h)/ZnS (48%) and CIS(8 h)/ZnS (85%) were caused by the effective passivation of the CIS core QDs surface by the ZnS shell. Generally, QDs growth is associated with surface defects. Therefore, the surface modification of QDs is very demanding and is achieved by growing an inorganic layer on the surface of QDs. ZnS passivation has been previously explored and was shown to improve luminescence QYs.

The powder XRD patterns of both CIS and CIS/ZnS are stacked, as shown in Fig. 3. The major diffraction peaks of the CIS core at 28.5°, 47.4°, and 55.5° can be attributed to the (112), (204)/(220), and (116)/(312) planes of a tetragonal chalcopyrite structure of the CIS phase and matched well with the JCPDS card 10-0216. Overcoating of the ZnS shell was conducted under the same condition for all CIS QDs. The XRD patterns of the two core/shell QDs after ZnS coating were identical. The diffraction peaks of the CIS/ZnS core/shell QDs shifted to a larger 2θ in contrast to those of the CIS QDs because the lattice parameter (a = 0.5517 nm) of the zinc blende ZnS is smaller than that of chalcopyrite CIS (a = 0.5345 nm). The diffraction patterns of the CIS/ZnS core/shell QDs were close to the (111), (220), and (311) planes of the zinc blende ZnS phase. Therefore, the ZnS layer coated the surface of the CIS QDs. The full-width-at-half-maximum of the CIS QDs was notably broader than those of the CIS/ZnS QDs in the XRD patterns, thereby suggesting that the cores of the CIS/ZnS QDs became larger than those of the CIS QDs. The difference between the absorption spectra and XRD-based nanocrystal sizes of the CIS and CIS/ZnS QDs might be explained by the alloying of CIS with ZnS during overcoating. CIS and ZnS have similar in terms of their crystallographic structure, Gibb formation enthalpy, and cation size, as reported by Park et al. The extended band gap of the CIS/ZnS QDs and the increased size of their cores in the present study were attributed to the generated CIS-ZnS alloyed...
phase on the core/shell interface.

To fabricate white LEDs with high CRI, the mixture of red-emitting CIS/ZnS QDs and yellow-emitting YAG:Ce phosphors was used to coat a blue chip (460 nm), as shown in Scheme I. The EL spectra of a blue LED chip that was solely coated with YAG:Ce phosphors and that of a blue LED chip with a mixture of red-emitting CIS/ZnS QDs and YAG:Ce phosphors under 20 mA forward bias current are shown in Fig. 4(a). Compared with the commercial YAG:Ce phosphor-based white LED, three emission bands were found in the fabricated CIS/ZnS QDs-assisted YAG:Ce phosphor-based white LED, which were located at 460, 560, and 625 nm and can be assigned as the emission bands of the blue chip, YAG:Ce phosphors, and CIS/ZnS QDs, respectively.

Generally, the CRI is a quantitative measure of the ability of a light source in contrast to that of a natural light source. The CRI value is designated by the symbol $R_a$ which represents the average value of $R_1$ to $R_8$. Numbers in the column indicate the Munsell hues in the Munsell color system. Therefore, the CRI of both the CIS/ZnS QDs-assisted YAG:Ce phosphor-based white LEDs and the commercial YAG:Ce phosphor-based white LEDs performed under a 20 mA forward bias current, as shown in Fig. 4(b). As compared with the commercial YAG:Ce phosphor-based white LEDs with $R_a = 75$, the CIS/ZnS QDs-assisted YAG:Ce phosphor-based white LED exhibited a higher $R_a$ of 86. The CRI was enhanced by the broader emission wavelength of the combined CIS/ZnS QDs. Consequently, an extensive spectral coverage of white light was generated. The obtained CRI were due to the improved values of $R_1$ and $R_8$, which resulted from the addition of the CIS/ZnS QDs. Meanwhile, CRI $R_9$ expressed the enhanced color

**Scheme I**  Schematic diagram of the fabrication of red-emitting CIS/ZnS QDs-assisted yellow-emitting YAG:Ce phosphor-based white LEDs

![Scheme I](image)

![Fig. 4](image)

**Fig. 4.** (a) EL spectra of commercial LEDs and LEDs with the additional CIS/ZnS QDs as converter materials. Inset shows photographs of CIS/ZnS QDs-assisted YAG:Ce phosphor-based white LEDs. (b) CRI of an as-fabricated CIS/ZnS QDs-assisted YAG:Ce phosphor-based white LED and a commercial YAG:Ce phosphor-based white LEDs under a forward bias current of 20 mA. (c) CIE chromaticity diagram for commercial LEDs (A: (0.3001, 0.3163)) and LEDs with additional CIS/ZnS QDs as converter materials (B: (0.3370, 0.3073)).
rendering of a deep-red region from 5 to 90. The commercial YAG:Ce phosphor-based white LEDs and the white LEDs with the red-emitting CIS/ZnS QDs and yellow-emitting YAG:Ce phosphors showed CIE color coordinates of (0.3001, 0.3163) and (0.3370, 0.3073), respectively, as shown in Fig. 4(c).

The PL bands of the CIS/ZnS QDs-assisted YAG:Ce phosphor-based white LEDs increased as the applied forward current increased from 20 mA to 120 mA, as shown in Fig. 5(a). Nevertheless, the optical properties of the CIS/ZnS QDs-assisted YAG:Ce phosphor-based white LEDs were changed under increasing applied forward current. The color coordinates of the white light were blue-shifted by the increasing forward current. This effect was accompanied by the variations of CRI values, thereby indicating that the QDs emission became relatively saturated with the increasing current bias, as shown in Fig. 5(b). The luminous efficiency dropped from 43.7 lm/W at 20 mA to 21.2 lm/W at 120 mA. Song et al. found that the bare blue chip has suffers from an intrinsic efficiency drop under increasing forward current. In the current study, the luminous efficiency of the CIS/ZnS QDs-assisted YAG:Ce phosphor-based white LEDs decreased because of this intrinsic property of the blue chip under the increasing forward current.

CONCLUSIONS

In conclusion, non-toxic CIS/ZnS QDs were successfully synthesized by the solvothermal method. Depending on the growing time of the core CuInS2 QDs, orange and red-colored CIS/ZnS QDs were generated with high QYs of 48% and 85%, respectively. Red-emitting CIS/ZnS QDs blended with YAG:Ce phosphors that were dispensed onto blue chips produced efficient white LEDs with a high CRI value (Ra = 86) as compared with the commercial YAG:Ce phosphor-based white LEDs. Furthermore, the EL properties were investigated in detail, such as the intensity and luminous efficiency under various forward currents. Luminous efficiency of 43.7 lm/W could be achieved at forward current of 20 mA.

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