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Bright three-band white light generated from CdSe/ZnSe quantum dot-assisted $Sr_3SiO_5:Ce^{3+},Li^+$-based white light-emitting diode with high color rendering index

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In this study, bright three-band white light was generated from the CdSe/ZnSe quantum dot (QD)-assisted $Sr_3SiO_5:Ce^{3+},Li^+$-based white light-emitting diode (WLED). The CdSe/ZnSe core/shell structure was confirmed by energy dispersive x-ray spectroscopy and x-ray photoelectron spectroscopy. The CdSe/ZnSe QDs showed high quantum efficiency (79%) and contributed to the high luminous efficiency (η_L) of the fabricated WLED. The WLED showed bright natural white with excellent color rendering property (η_L=26.8 lm/W, color temperature=6140 K, and color rendering index=85) and high stability against the increase in forward bias currents from 20 to 70 mA. © *2009 American Institute of Physics*. [doi:10.1063/1.3246800]

Lighting devices are very prevalent in our life and we see them everyday in our homes, offices, laboratories, etc. The large amount of energy needed for illumination is generated from the consumption of fossil fuels which generate CO_2 gas, a leading cause of global warming.[1] Therefore, new light sources which contribute to energy saving is necessary. In the case of white light-emitting diodes (LEDs), since they have high conversion efficiency from electric energy to visible light, long life time, and reliability, etc., they are a promising next generation illumination source.[2,3] Also they have the advantage of being environmentally benign because they do not contain mercury gas. Among the various types of white LEDs (WLEDs), phosphor-converted (pc) WLEDs are becoming more popular in the illumination field due to advantages, such as high luminous efficiency, simple structure, and relatively low cost compared to multichip WLEDs.[4] Recently, Ce^{3+}-doped yttrium aluminum garnet (YAG:Ce)-based WLEDs have been commercialized.[5] However, since the color rendering property of YAG:Ce-based WLED is not good due to the red deficiency of the YAG:Ce phosphor, many researchers have studied to improve the color rendering property of pc WLEDs.[6–9] Besides inorganic phosphors, quantum dots (QDs) can be an alternative downconverter in the WLED. Semiconductor nanocrystals have been attractive to scientists since the pioneering works of Ekimov *et al.*[10] in doped glasses and Rossetti *et al.*[11] in colloidal nanoparticles. In particular, CdSe QDs have been extensively researched since Murray *et al.*[12] reported monodisperse CdSe QDs. In the case of CdSe QDs, desired emission wavelength can be easily manipulated by adjusting the particle size (quantum confinement effect) and CdSe QDs show higher emission efficiency compared to bulk CdSe.[13] Recently, we reported organically capped CdSe QD-assisted $Sr_3SiO_5:Ce^{3+},Li^+$ (SSCL) phosphor-based WLED with excellent color rendering property.[14] In our previous study, although the color rendering property of the fabricated WLED was excellent, the luminous efficiency of the WLED was lower than that of SSCL-converted WLED. If luminescence of CdSe QDs is enhanced, the CdSe QD-assisted SSCL-based WLED will show higher luminous efficiency. Hines and Guyot-Sionnest,[15] Dabbousi *et al.*,[16] and Peng *et al.*[13] obtained highly luminescent CdSe QDs using core/shell structure such as CdSe/ZnS and CdSe/CdS. In addition, Reiss *et al.*[17] used ZnSe as a shell material due to its low lattice mismatch with CdSe and the same anion (Se^{2-}). Therefore, we synthesized CdSe/ZnSe core/shell QDs to enhance the emission intensity of CdSe QDs and applied them to WLEDs. In this study, the growth of the ZnSe shell on the CdSe core was confirmed by characterizing with energy dispersive x-ray spectroscopy (EDS) and x-ray photoelectron spectroscopy (XPS). The CdSe/ZnSe core/shell QD-assisted SSCL-based WLED was fabricated and it showed high luminous efficiency with high color rendering index (R_a) indicating that the WLED is acceptable to general illumination.

To fabricate a bright WLED with high R_a value, the greenish-yellow-emitting SSCL phosphor in which Ce^{3+} concentration is 0.8 mol % and red-emitting CdSe/ZnSe QDs were synthesized. The SSCL phosphor was synthesized by using a solid state reaction method in a reducing atmosphere.[2] The CdSe/ZnSe QDs were synthesized by using modified organometallic synthesis method.[14,17] Cadmium acetate dihydrate [$(CH_3CO_2)_2Cd.2H_2O$, 98%], zinc acetate [$(CH_3CO_2)_2Zn$, 99.99%], selenium (99.99%), technical grade trioctylphosphine (TOP), technical grade trioctylphosphine oxide (TOPO), and hexadecylamine (HDA, 90%) were purchased from Aldrich. Since diethyl zinc, one of the most popular Zn source, is very toxic and dangerous,[18] in this study $(CH_3CO_2)_2Zn$ was used as a Zn precursor. $(CH_3CO_2)_2Zn$ was complexed with TOP and then mixed with TOPSe and TOP solution. The mixture of TOPZn/TOPSe/TOP was slowly injected into a mixture of TOPO/HDA containing CdSe core nanoparticles (~50 μl/min).

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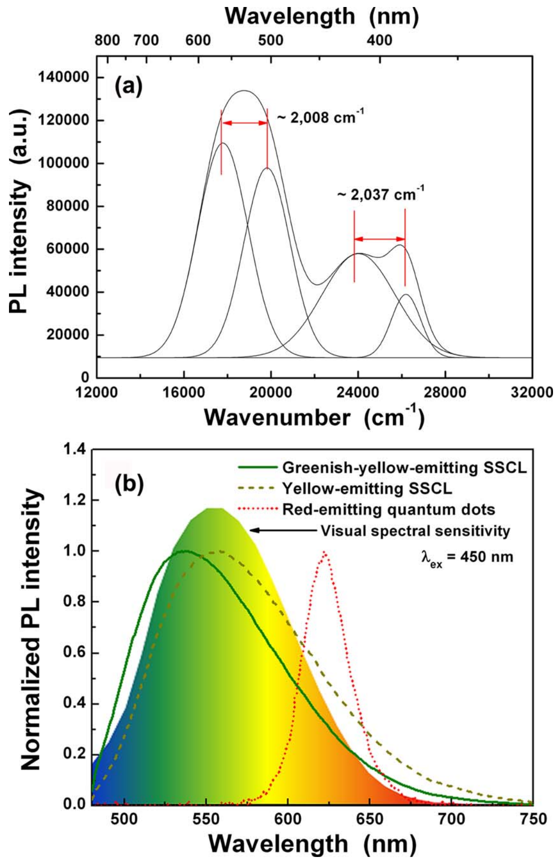

FIG. 1. (Color online) (a) Low temperature PL spectrum of SSCL phosphor. (b) Normalized PL spectra of greenish-yellow-emitting SSCL (solid line), yellow-emitting SSCL (broken line), and red-emitting CdSe QDs (dotted line).

The injection was performed at 150 °C to prevent additional growth of CdSe core nanocrystals. The WLED was fabricated by combining blue LED ($\lambda_{peak}=455$ nm) with the mixture of the SSCL phosphor and CdSe/ZnSe QDs, and its optical properties were investigated under operating at 20 mA. An integrating sphere was used to obtain luminous efficiency and current stability was also investigated against the increase in the forward current from 20 to 70 mA.

Figure 1 shows the photoluminescence (PL) spectra of SSCL phosphor and red-emitting CdSe QDs. Figure 1(a) depicts a PL spectrum of greenish-yellow-emitting SSCL phosphor under the excitation of 325 nm at 7 K. In the case of Ce^{3+}, ground 4*f* level is split into two sublevels ($^2F_{7/2}$ and $^2F_{5/2}$) by spin-orbit coupling.[19] These two emission bands, shown in Fig. 1(a), are attributed to the transitions of $^2D_{3/2} \rightarrow {}^2F_{7/2}$ and $^2F_{5/2}$, and $^2D_{5/2} \rightarrow {}^2F_{7/2}$ and $^2F_{5/2}$, respectively.[2] From the PL spectrum, the energy differences between $^2F_{7/2}$ and $^2F_{5/2}$ are calculated to be 2008 and 2037 cm^{-1}, which are well-matched with the theoretical value (~ 2000 cm^{-1}). Thanks to this spin-orbit coupling, the SSCL phosphor shows a very broad emission band.[2] As shown in Fig. 1(b), although the SSCL phosphor shows a broad yellow band, red spectral intensity is relatively weak. The human eyes are insensitive to red light in the spectral region above 675 nm [see Fig. 1(b) visual spectral sensitivity curve]. Thus, the enhancement in the red spectral range between 600 and 650 nm effectively improves the color rendering property. Red spectral intensity in this range can be enhanced by the addition of highly luminescent red-emitting QDs. It was shown in our previous

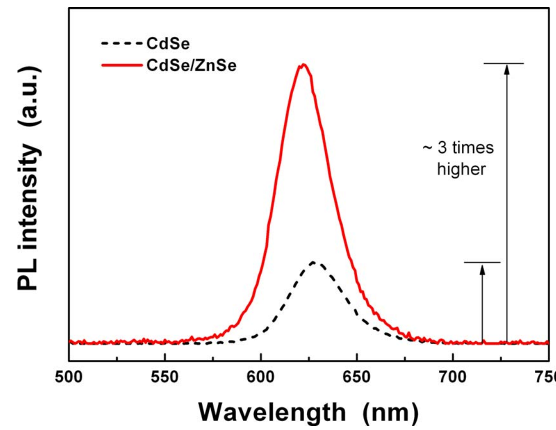

FIG. 2. (Color online) PL spectra of CdSe core and CdSe/ZnSe core/shell QDs.

report that the peak wavelength of the SSCL phosphor can be tuned by controlling the concentration of Ce^{3+} ions.[4] Thus, when the greenish-yellow-emitting SSCL phosphor is combined with red-emitting QDs, the WLED fabricated with them covers a wider visible spectral range and may have more excellent color rendering property than the yellow-emitting SSCL-based WLED.

Figure 2 shows the PL spectra of CdSe and CdSe/ZnSe QDs. From the literature,[17] when the shell thickness was 1.8 ML, CdSe/ZnSe QDs showed large emission enhancement. Therefore, our CdSe QDs were coated with 1.8 ML of ZnSe. As shown in Fig. 2, emission intensity of CdSe/ZnSe QDs is approximately three times higher than that of CdSe QDs. The quantum efficiencies (QEs) of CdSe core and CdSe/ZnSe core/shell were measured to be 23% and 79%, respectively. If the core CdSe is overcoated with a wide band gap material without alloying, the emission band shifts to a longer wavelength.[13] In this experiment, the emission band did not show redshift but shifted slightly to a shorter wavelength (627 nm for CdSe → 623 nm for CdSe/ZnSe). This means that an alloying compound was formed. According to Lee *et al.*,[20] when the alloying compound, i.e., $Cd_{1-x}Zn_xSe$, was formed, the emission peak shifted to a shorter wavelength with increasing Zn concentration. Thus, it is believed that the alloying compound was formed at the interface between CdSe core and ZnSe shell, judging from the PL spectra.

Figure 3 insets show the high resolution transmission electron microscopy (HR-TEM) images of CdSe and CdSe/ZnSe QDs. The clear lattice fringe image of the synthesized CdSe/ZnSe is shown in the HR-TEM image. However, the interface of CdSe and ZnSe is ambiguous. Although the boundary between CdSe core and ZnSe shell is not distinguishable in the HR-TEM image, it is certain that ZnSe is present on the CdSe surface from the presence of Zn-related peaks in an EDS spectrum of Fig. 3(b).

In addition, XPS results shown in Fig. 4 support the formation of ZnSe shell. XPS was performed using an ESCALAB 250. The binding energies in the XPS spectra were calibrated using that of C 1*s* (284.6 eV). The presence of C and O originates primarily from atmospheric contamination during the brief exposure of the samples to air.[16] As expected, the XPS lines from Zn, in addition to the Cd and Se lines, were detected in the CdSe/ZnSe QD. Thus, the HR-TEM image combined with EDS and XPS results provides proof of a crystalline shell. A weak phosphorous line at about

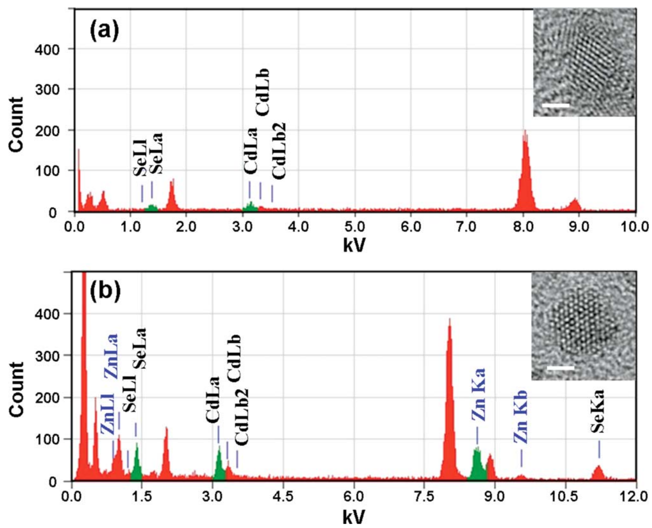

FIG. 3. (Color online) EDS spectra of (a) CdSe core and (b) CdSe/ZnSe. Insets are HR-TEM images of CdSe and CdSe/ZnSe, respectively (scale bar: 2 nm).

140 eV was detected on both the CdSe and indicating the presence of residual TOPO/TOP molecules bound to Cd or Zn on the nanocrystal surface.[16]

Figure 5 shows the electroluminescence (EL) spectra and the Commission Internationale de l'Eclairage (CIE) color coordinates of CdSe/ZnSe QD-assisted SSCL-based WLEDs under the various forward bias currents of 20, 30, 40, 50, 60, and 70 mA, respectively. The optical properties of the WLED were evaluated at 20 mA and the WLED showed a luminous efficiency (η_L) of 26.8 lm/W, which is much higher than the luminous efficiency of CdSe QD-assisted SSCL-based WLED ($\eta_L = 14.0$ lm/W), color temperature (T_c) of 6140 K, and R_a of 85. The CdSe/ZnSe QD-assisted SSCL-based WLED showed increased luminous intensity without luminescence saturation against the increase in forward currents. Although the forward current was increased from 20 to 70 mA, the CIE color coordinates of the WLED hardly changed [(0.3185, 0.3414) at 20 mA $\rightarrow$(0.3146, 0.3442) at 70 mA]. On the other hand, YAG:Ce-based WLED showed large variation in the CIE color coordinates with increasing the forward current as expressed by the open triangle in Fig. 5(b). This result demonstrates the high stability of the WLED fabricated in this study.

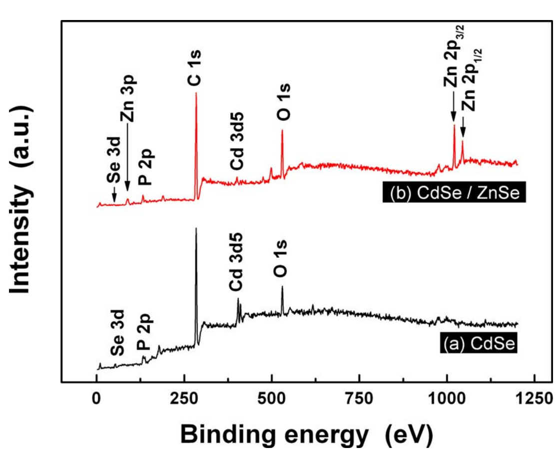

FIG. 4. (Color online) XPS spectra of (a) CdSe core and (b) CdSe/ZnSe core/shell.

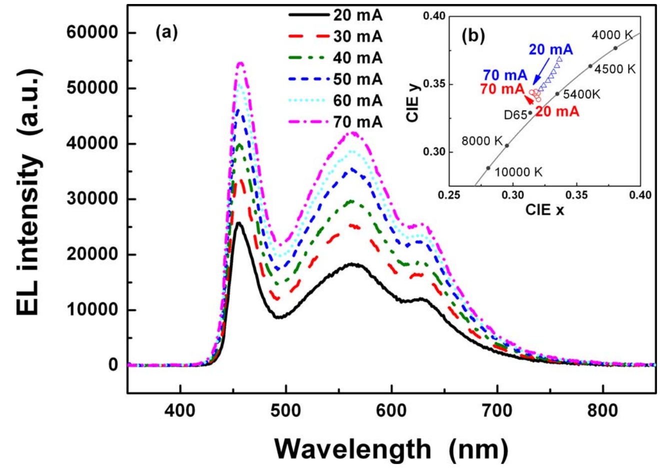

FIG. 5. (Color online) (a) EL spectra and (b) CIE color coordinates of the CdSe/ZnSe QD-assisted SSCL-based WLED under various forward bias currents from 20 to 70 mA (○: CdSe/ZnSe QD-assisted SSCL-based WLED and △: YAG:Ce-based WLED).

In summary, greenish-yellow-emitting SSCL phosphor and highly luminescent CdSe/ZnSe QDs were synthesized. The ZnSe shell was grown on the CdSe core and it contributed to the increase in the QE of the CdSe. The CdSe/ZnSe QD-assisted SSCL-based WLED was fabricated and it fully covered visible spectral range with its emission band consisting of three subbands from the blue LED, SSCL phosphor, and CdSe/ZnSe QDs. The fabricated WLED emitted bright natural white light with excellent color rendering property ($\eta_L = 26.8$ lm/W, $T_c = 6140$ K, and $R_a = 85$). Also, it showed stable white light against the large increase in forward bias currents.

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