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Phosphine-Free-Synthesized ZnSe/ZnS Core/Shell Quantum Dots for White Light-Emitting Diodes

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Abstract: Blue-light-emitting ZnSe core (C) and ZnSe/ZnS core/shell (C/S) quantum dots (QDs) were synthesized with phosphine-free precursors by a thermal decomposition method in paraffin oil solvent and applied to QD-converted light-emitting diodes (LEDs). The optical properties of the synthesized ZnSe C and ZnSe/ZnS C/S QDs were characterized by absorption spectroscopy and photoluminescence spectroscopy. Additionally, the quantum efficiency of the QDs was investigated. Their structural properties were studied with X-ray crystallography and transmission electron microscopy. The ZnSe/ZnS C/S QDs showed deep-blue light peaking at 425 nm. The blue-light-emitting ZnSe/ZnS C/S QDs were used as color-converting materials for near-ultraviolet LED-pumped blue LEDs and combined with yellow-light-emitting Zn-Cu-In-S/ZnS C/S QDs to fabricate white LEDs. The white LEDs showed warm white light [(CIE x, CIE y) = (0.4088, 0.3987)], T_c = 3488 K, and R_a = 61.2]. The results indicate that the ZnSe/ZnS C/S QDs have good potential for white light application after further improvements to their optical properties.

Keywords: ZnSe/ZnS quantum dots; core/shell structure; blue LED; warm white LED

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1. Introduction

Nanometer-scaled semiconductor materials called quantum dots (QDs) exhibit size-dependent electronic and optical properties due to the quantum confinement effect that is generated from spatially driven charge carriers, including holes and electrons in the ground and excited states [1–3]. Colloidal QDs are widely used in solar cells, biolabeling, light-emitting diodes (LEDs), CO_2 reduction in water, and radioluminescent nuclear batteries [4–8]. In the last three decades, cadmium-based QDs have been popular, especially for light-emitting diode and display applications, due to their superior properties, such as size-controlled emission wavelengths over the entire visible light range, narrow and symmetric emission spectra, high photoluminescence (PL) quantum yields (QYs), and high photostability [9,10].

However, there is now growing demand to develop cadmium-free QDs to reduce environmental harm and human health issues [11]. Related to these issues, cadmium-free green- or red-light-emitting materials, such as InP, $CuInS_2$, Si-based QDs, and carbon dots, have been studied as alternatives to CdSe QDs [12–15]. Additionally, blue-light-emitting, ultra-small ZnSe-based QDs are one of the outstanding candidates for cadmium-free QDs and combining them with red- and green-emitting QDs can produce nonpoisonous white

LEDs. ZnSe QDs were first synthesized by arrested precipitation, and more recently, using reverse micelles, precipitation in the presence of stabilizers, and heating-up and hot-injection methods [16,17]. In the hot-injection method, a reagent at room temperature is injected into the hot-reaction solution, producing a burst and homogenous nucleation, followed by slow growth, and annealing of the nanoparticles [18]. In early works, ZnSe QDs were synthesized using trioctylphosphine (TOP), trioctylphosphine oxide (TOPO), and tributylphosphine (TBP) as the solvent and stabilizing ligands [19,20]. Highly luminescent ZnSeTe-based QDs have been recently reported and applied to electroluminescent devices [21,22]. In those studies, TOP was also used to synthesize ZnSeTe-based QDs. In recent years, researchers have avoided using these toxic and expensive chemical reagents [23]. For example, in a previously reported method, zinc precursor was injected into paraffin oil containing Se-ODE at high reaction temperature [23].

In this study, we focused on synthesizing eco-friendly ZnSe-based QDs using phosphine-free precursors. The ZnSe C QDs were synthesized without phosphine precursors and the ZnSe/ZnS C/S QDs were also synthesized with phosphine-free precursors via the one-pot synthesis method to improve their PL properties. There are many kinds of zinc source materials that can be used as zinc precursors, including zinc acetate, zinc stearate, diethyl zinc, and zinc oxide, depending on the synthesis environment [23–26]. In this study, we used ZnO, which is soluble in acids and alkalis and can form complexes with ligands containing O-, N-, or S-donor atoms [27]."Zn-oleate precursors were prepared by reacting ZnO and OA in paraffin oil. To synthesize high-quality and Cd-free, blue-emitting ZnSe QDs, we investigated the effects of reaction time and temperature on the PL properties of the ZnSe QDs.

In addition, we investigated the applicability of the ZnSe/ZnS C/S QDs as color-converting materials in optoelectronic devices such as LEDs. The phosphine-free synthesized blue-light-emitting ZnSe/ZnS C/S QDs were used as color-converting materials for near ultraviolet (nUV) LED-pumped blue LEDs. We also investigated the applicability of the ZnSe/ZnS C/S QDs to white LEDs. White LEDs are in high demand in the lighting and display fields because of their notable properties, including non-toxicity (no mercury), low power consumption, and long operating time [28,29]. For the first time, blue-light-emitting ZnSe/ZnS C/S QDs and yellow-light-emitting, Zn-doped $CuInS_2$/ZnS C/S QDs were combined to fabricate white LEDs. The $CuInS_2$-based QDs are suitable for white LED applications thanks to their high chemical stability, non-toxicity, tunable emitting wavelength, high luminous efficiency, large optical absorption coefficient, and large Stokes shift [30,31]. For these reasons, $CuInS_2$/ZnS-based QDs were adopted as the yellow-emitting materials. This study demonstrated that the ZnSe/ZnS QDs are promising for use as a color-converting material for the fabrication of white LEDs.

2. Materials and Methods

Materials. To synthesize the ZnSe/ZnS C/S QDs, zinc oxide (ZnO, 99.99%), selenium (Se, 99.99%), sulfur (S, 99.9%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%), hexane (95%), chloroform (95%), paraffin oil (analytical grade), acetone (analytical grade), and ethanol (EtOH, analytical grade) were purchased from Sigma-Aldrich. To synthesize the Zn-doped $CuInS_2$/ZnS (ZCIS/ZnS) C/S QDs, copper (I) iodide (CuI, 99.999%), indium acetate ($C_6H_9InO_6$, 99.99%), zinc chloride ($ZnCl_2$, ≥98%), and 1-octanethiol (OTT, ≥98.5%) were purchased from Sigma-Aldrich. Sodium oleate ($C_{18}H_{33}NaO_2$, >97.0%) was purchased from Tokyo Chemical Industry.

Preparation of the Zn precursor. Two mmol of ZnO, OA (4.5 g), and paraffin oil (14 mL) were loaded in a three-neck flask and heated to 300 °C for 30 min under argon flow to obtain a colorless, clear solution. After the reaction was finished, the temperature was cooled to room temperature and the resulting Zn-oleate precursors were stored in an argon atmosphere.

Preparation of the Se precursor. Two mmol of Se and ODE (20 mL) were loaded in a three-neck flask and heated to 220 °C for 180 min under argon flow. After the reaction was

complete, the temperature was cooled to room temperature and the Se precursors were stored in an argon atmosphere.

Preparation of the S precursor. For preparation, 2 mmol of S and ODE (20 mL) was loaded in a three-neck flask and heated to 150 °C for 30 min under argon flow. After the reaction was complete, the temperature was cooled to room temperature and the S precursors were stored in an argon atmosphere.

Synthesis of the ZnSe/ZnS C/S QDs. ZnSe/ZnS C/S QDs were synthesized via a hot-injection method with a slight modification of the previously reported method [23]. Two mL Se precursor and 4.5 mL paraffin oil were loaded in a 50 mL, three-neck flask and heated to 115 °C for 30 min under a vacuum. After the solution was degassed, the reaction temperature was increased to 310 °C under argon gas flow. Three mL of the Zn precursor solution was injected swiftly, and the temperature was kept at 310 °C for 1 h for ZnSe growth. To grow the ZnS shell on the ZnSe core, 1 mL of the S precursor was slowly injected dropwise into the core solution at 310 °C. At intervals of 10 min, 1 mL of the Zn precursor was injected dropwise into the core solution. After aging for 30 min under argon gas, the synthesized ZnSe/ZnS C/S QDs were washed with acetone, acetone/EtOH, and EtOH and finally dispersed in hexane for further study. Aliquots were taken at different time intervals to investigate growth kinetics by optical property characterization, such as UV-vis absorption and PL spectroscopy.

Synthesis of the Zn-doped $CuInS_2$/ZnS (ZCIS/ZnS) C/S QDs. The ZCIS/ZnS C/S QDs were synthesized via a hot-injection method with a slight modification of the previous method [32]. Typically, a mixture of CuI (0.0238 g, 0.125 mmol), $In(Ac)_3$ (0.1459 g, 0.5 mmol), Zn-oleate (0.0126 g, 2 mmol), and 5 mL ODE was loaded in a three-neck flask and heated to 120 °C for 30 min under a vacuum. After the solution was degassed, the reaction temperature was increased to 230 °C under argon gas flow. Three mL of OTT was swiftly injected, and the temperature was kept at 230 °C for 10 min. A mixture of Zn stearate (2.5294 g, 4 mmol), 4 mL OA, and 2 mL ODE was injected dropwise into the reaction flask. After the injection of the Zn precursors, the reaction temperature was increased to 240 °C and kept for 270 min. The synthesized ZCIS/ZnS C/S QDs were washed with EtOH and dispersed in hexane for further use.

Fabrication of the ZnSe/ZnS QD-converted blue LEDs. To fabricate the nUV LED-pumped ZnSe/ZnS C/S QD-converted blue LEDs, the ZnSe/ZnS C/S QDs were redispersed in 3 mL $CHCl_3$ (optical density ~ 1.892 at 365 nm) and the solution was mixed with silicone resin mixture (0.2074 g, OE-6630B:OE-6630A = 4:1, Dow Corning Co., Midland, MI, USA). The silicone–QD blend was degassed under a vacuum to remove the $CHCl_3$ and air bubbles. The mixture of ZnSe/ZnS C/S QDs and silicone resin was coated on 395 nm nUV LEDs (non-molded, surface-mounted-device (SMD) type, 5.0 × 5.0 mm^2). The nUV LED packages, encapsulated with ZnSe/ZnS C/S QD–silicone resin, were cured at 60 °C for 60 min, followed by curing at 110 °C for 60 min.

Fabrication of the blue and yellow QD-converted white LEDs. To fabricate the ZnSe/ZnS and ZCIS/ZnS QD-converted white LED, the ZnSe/ZnS and ZCIS/ZnS QDs were redispersed in $CHCl_3$ (optical density of ZnSe/ZnS ~ 2 at 365 nm and ZCIS/ZnS ~ 0.544 at 450 nm) and the 3 mL QD $CHCl_3$ solution was mixed with silicone resin (0.4019 g, OE-6630B:OE-6630A = 4:1). The QDs and silicone mixture was degassed under a vacuum to remove the $CHCl_3$ and air bubbles. The final ZnSe/ZnS QDs and ZCIS/ZnS QD–silicone resin mixture was coated on a 395 nm-emitting nUV LED chip (non-molded 5.0 × 5.0 mm^2 SMD type). The white LED packages encapsulated with ZnSe/ZnS and ZCIS/ZnS–silicone resin were cured at 60 °C for 60 min, then at 110 °C for 60 min.

Characterization. The PL and absorption spectra of the ZnSe-based QDs were collected with a Hitachi F-7000 spectrophotometer and a PerkinElmer LAMBDA 25 spectrophotometer, respectively. Transmission electron microscopy (TEM) was conducted with a Tecnai G2 F20 scanning transmission electron microscope operated at 200 kV to investigate the size and morphologies of the QDs. The particle sizes of the ZnSe C QDs and ZnSe/ZnS C/S QDs were determined by measuring one hundred of the QDs in the TEM

images. X-ray diffraction (XRD) was performed with a Bruker D8 ADVANCE operated at 40 kV and 40 mA ($\lambda_{CuK\alpha}$ = 1.5406 Å) to analyze the crystal structure of the QDs. The absolute PL quantum yields (QYs) of the ZnSe C QDs and ZnSe/ZnS C/S QDs were measured with a QE-1100 quantum efficiency measurement system (Otsuka Electronics Co., Ltd., Osaka, Japan) using an integrating hemisphere. Optical properties, including electroluminescence (EL) spectra, Commission Internationale de l'Éclairage (CIE) color coordinates, color rendering index (R_a), and the correlated color temperature (T_c) of the white LEDs, were evaluated using an OPI-100 total luminous flux measurement system (Withlight Co., Ltd., Jeonju, Korea).

3. Results and Discussion

The growth of the ZnSe C QDs was investigated by absorption spectra, as shown in Figure 1a. The first absorption peak was observed at 407 nm for the aliquot taken at 5 min and continuously redshifted to 418 nm as the reaction time increased. This shift resulted from the increase in core size, and it indicated a size-dependent, electronic-energy band structure [33]. Consequently, a redshift in the absorption spectra of the ZnSe C QDs was observed with the growth of the ZnSe due to quantum confinement effects [33]. PL spectra also shifted from 413 nm to 425 nm with increasing reaction time. The absolute PL QY of the ZnSe C QDs was measured to be 19.4%. As the reaction time increased, the bandwidth of the ZnSe C QDs became narrower. The full width at half-maximum (FWHM) of the PL band of the ZnSe C QDs was 15.5 nm for the aliquot taken at 5 min and 13.5 nm for the aliquot taken at 60 min, which indicates that size focusing occurred during the growth of the ZnSe C QDs. The synthesized ZnSe C QDs exhibited narrow size distribution (4.6 ± 0.2 nm, average size ± standard deviation).

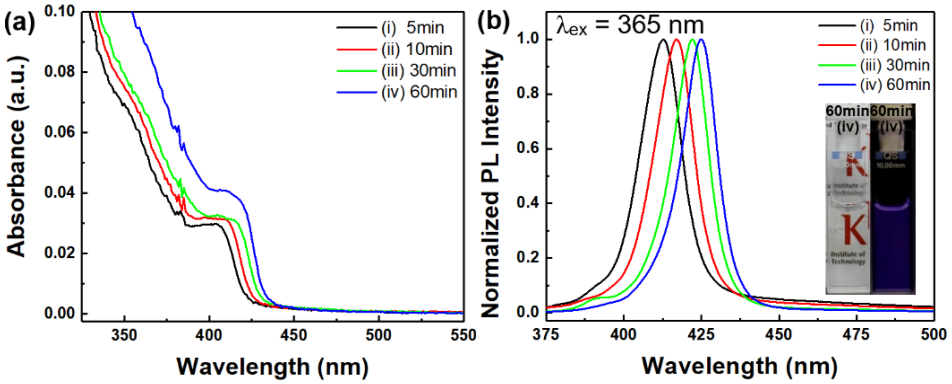

Figure 1. (**a**) Absorption and (**b**) PL spectra of the as-synthesized ZnSe C QDs as a function of reaction time ((i) 5 min, (ii) 10 min, (iii) 30 min, and (iv) 60 min)). The inset in (**b**) shows photographs of the ZnSe C QD solution (reaction time was 60 min) under indoor light (left) and UV light (right, λ = 365 nm).

The photophysical properties of the synthesized ZnSe C QDs can be improved by the formation of a ZnSe/ZnS C/S structure, since the ZnS shell decreases surface defects and increases confinement of the exciton [3,34]. The effect of ZnS shelling on the optical properties of the ZnSe QDs was investigated (Figure 2a,b). Figure 2a shows the absorption spectra of ZnSe C and ZnSe/ZnS C/S QDs. The formation of the ZnS shell on the ZnSe core decreased the surface defects of the ZnSe core [16]; thus, PL intensity increased, as shown in Figure 2b. The absolute PL QY of the ZnSe/ZnS C/S QDs was measured to be 37.4%. The ZnSe/ZnS C/S QDs exhibited their first absorption peak at different wavelengths, depending on the reaction temperature of the ZnSe/ZnS C/S QDs. The reaction temperature was increased from 310 °C to 330 °C, and absorption peaks were observed at 421 nm, 423 nm, and 427 nm for the ZnSe/ZnS C/S QDs synthesized at 310 °C, 320 °C, and 330 °C, respectively (Figure 3a). Since increasing the reaction temperature affected nucleation and growth of the QDs, larger QDs could be synthesized at higher reaction temperatures and a

redshift of the absorption band was observed due to the quantum confinement effect [23]. Figure 3b shows that the PL intensity of the ZnSe/ZnS C/S QDs synthesized at 310 °C was higher than those of the ZnSe/ZnS C/S QDs synthesized at 320 °C and 330 °C. As the temperature was increased from 310 °C to 320 °C and 330 °C, PL intensity decreased. According to Peng's group, the PL QY of the QDs depends on the sizes of the QDs [35]. Thus, it is believed that, when the temperature is 320 °C, the size of the ZnSe/ZnS C/S QDs is larger than the optimal size of the ZnSe/ZnS C/S QDs, which shows the best PL property. When the ZnSe/ZnS C/S QDs were synthesized at 300 °C, blue light was hardly observed. As a consequence, the optimized reaction temperature in this study was 310 °C.

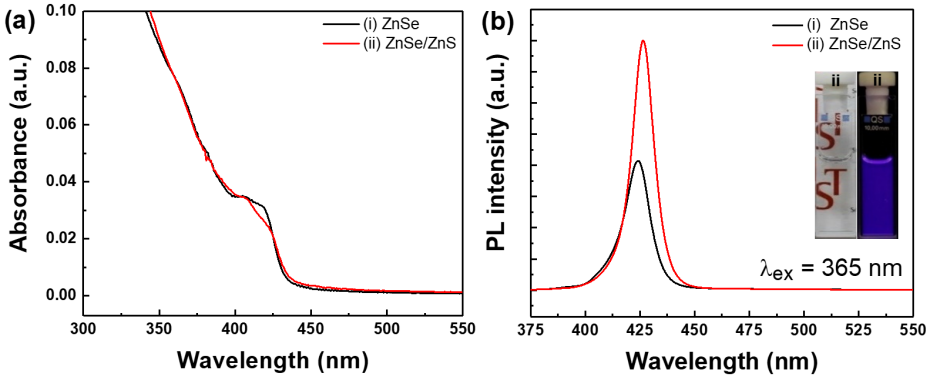

Figure 2. (**a**) Absorption and (**b**) PL spectra of (i) ZnSe C QDs and (ii) ZnSe/ZnS C/S QDs synthesized at 310 °C. The inset in (**b**) shows photographs of the ZnSe/ZnS C/S QD solution under indoor light (left) and UV light (right, λ = 365 nm).

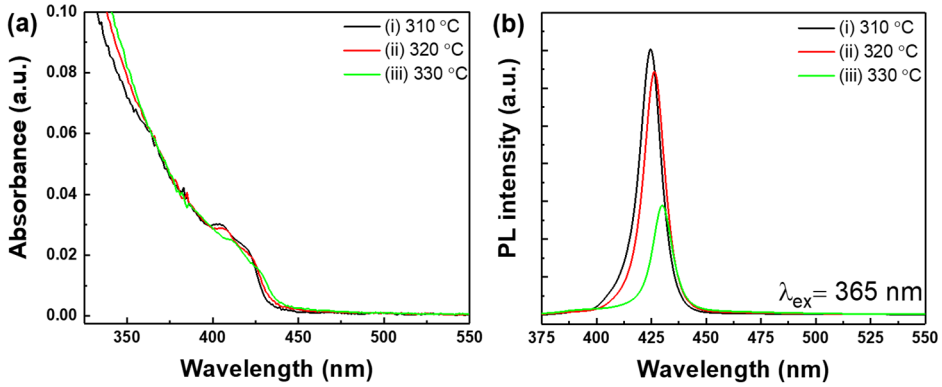

Figure 3. (**a**) Absorption and (**b**) PL spectra of the ZnSe/ZnS C/S QDs synthesized at (i) 310 °C, (ii) 320 °C, and (iii) 330 °C, respectively.

In addition to spectroscopic studies, XRD patterns and TEM images were obtained to investigate the structure of the ZnSe C and ZnSe/ZnS C/S QDs in which ZnSe C was synthesized at 310 °C for 1 h and the ZnS shell was formed by heat treatment at 310 °C for 50 min. As shown in the XRD pattern, the peak positions of the ZnSe C QDs were in agreement with bulk ZnSe with a zinc blende structure (Figure 4a-i). Three obvious diffraction peaks located at 27.2°, 45.3°, and 53.5° corresponded to the diffraction peaks of the (111), (220), and (311) planes of zinc blende ZnSe, respectively. After the shelling procedure (Figure 4a-ii), the zinc blende structure remained and XRD peaks were slightly shifted to higher angles (27.6°, 46.1°, and 54.1°) because ZnS has smaller lattice parameters than ZnSe [36]. The high degree of crystallinity was also confirmed by high-resolution TEM (HR-TEM) images, shown in Figure 4b. The HR-TEM images and fast Fourier transformation (FFT) patterns of the ZnSe C and ZnSe/ZnS C/S QDs are shown in Figure 4b. The lattice fringes were separated by d = 0.32 nm for the ZnSe C and the ZnSe/ZnS C/S QDs, which was consistent with the lattice spacings between the (111)

planes of zinc blende ZnSe. The synthesized ZnSe/ZnS C/S QDs exhibited a narrow size distribution of 5.1 ± 0.5 nm (average size ± standard deviation).

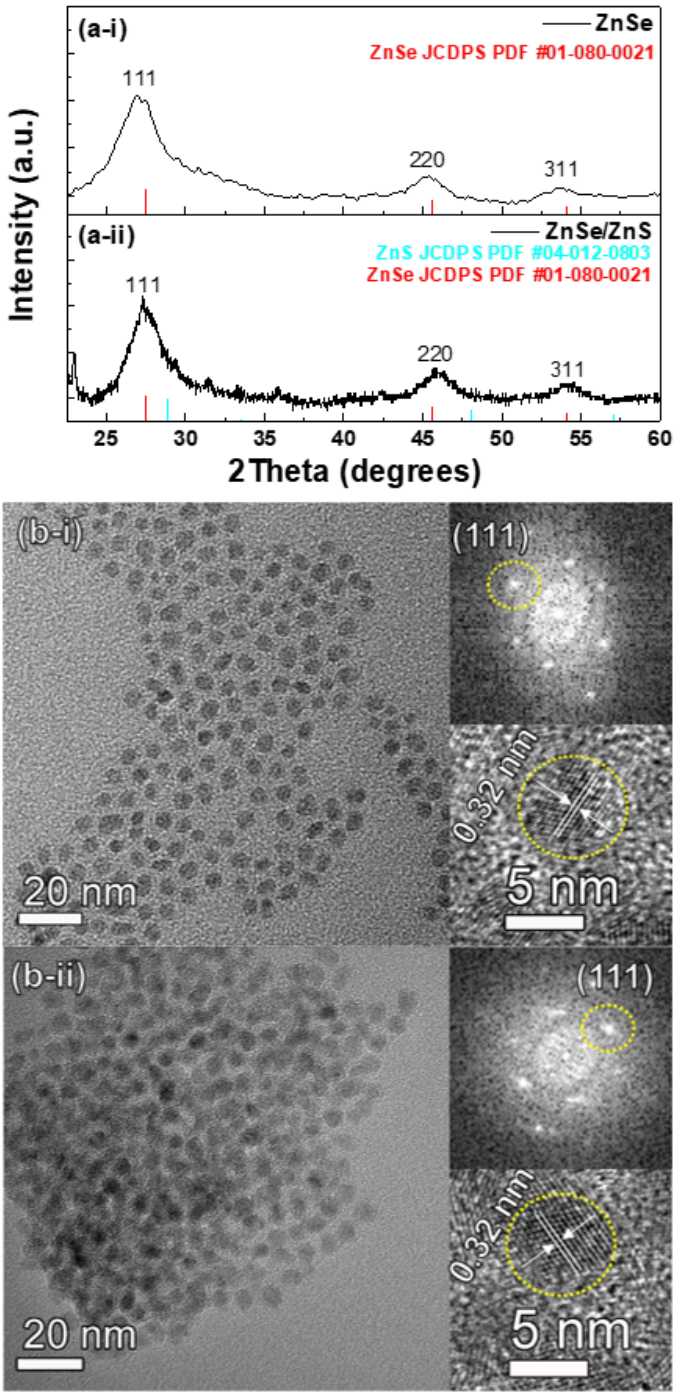

Figure 4. (**a**) XRD patterns and (**b**) TEM images of (**i**) ZnSe C QDs and (**ii**) ZnSe/ZnS C/S QDs. Lower insets in (**b**) show HR-TEM images of (**i**) ZnSe C QDs and (**ii**) ZnSe/ZnS C/S QDs and the upper insets in (**b**) show FFT patterns for the corresponding HR-TEM images.

nUV LED-pumped blue LEDs were fabricated with the ZnSe/ZnS C/S QDs. Figure 5 shows the optical properties of the fabricated blue LEDs, which were evaluated at 60 mA. In the EL spectrum, two peaks were observed. One peak in the nUV region and the other peak in the blue region were attributed to the nUV LED and ZnSe/ZnS C/S QDs, respectively. Blue light was emitted from the fabricated LED due to the strong EL peak in the blue

spectral region (Figure 5a inset). Moreover, the CIE chromaticity diagram shows that the color coordinates of the emission light from the ZnSe/ZnS C/S QD-converted LED were located in the blue region (Figure 5b).

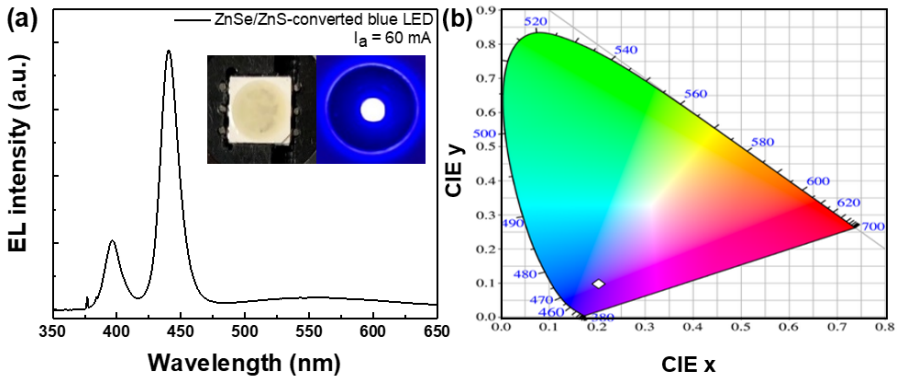

Figure 5. (**a**) EL spectra of the ZnSe/ZnS-converted blue LED at 60 mA and (**b**) CIE color coordinates of the ZnSe/ZnS-converted blue LED. The inset in (**a**) shows photographs of the ZnSe/ZnS-converted blue LED without (left) and with (right) applied current.

In addition to fabricating the ZnSe/ZnS C/S QD-converted blue LED, ZnSe/ZnS C/S QD-converted white LEDs were also fabricated. White light can be generated by combining blue-emitting ZnSe/ZnS C/S QDs with yellow-emitting QDs. We synthesized yellow-emitting ZCIS/ZnS C/S QDs by referring to the previous method with a slight modification [32]. As shown in Figure 6, the ZCIS/ZnS C/S QDs exhibited an absorption band in the blue spectral region and a broad PL band under 450 nm excitation. The ZCIS/ZnS C/S QDs showed a broad PL band peaking at 565 nm with a wide FWHM of 115.5 nm, resulting in yellow luminescence. The PL QY of the yellow-light-emitting ZCIS/ZnS C/S QDs was measured at 83%. The absorption band of the ZCIS/ZnS C/S QDs was well matched with the emission band of the ZnSe/ZnS C/S QDs. Thus, a combination of ZnSe/ZnS C/S QDs and ZCIS/ZnS C/S QDs can create white light.

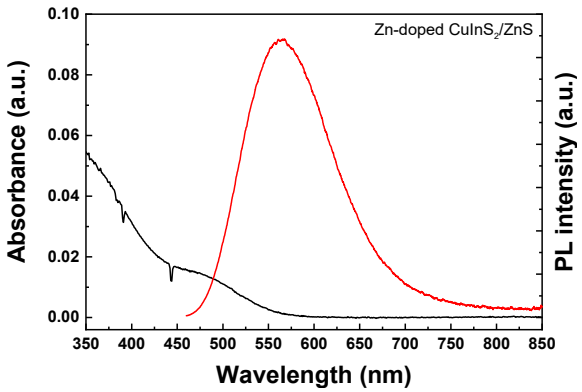

Figure 6. Absorption (black line) and PL (red line) spectra of Zn-doped $CuInS_2$/ZnS C/S QDs.

In this study, to investigate the applicability of ZnSe/ZnS C/S QDs for warm white LEDs, which can be used in the lighting field, we fabricated warm white LEDs by combining an nUV LED chip, ZnSe/ZnS C/S QDs, and ZCIS/ZnS C/S QDs. Figure 7 shows the optical properties of the warm white LEDs, which were evaluated at 60 mA. In the EL spectrum shown in Figure 7a, three peaks were observed. The peak in the nUV region is attributed to the nUV LED chip, and other peaks in the blue and yellow spectral regions are attributed to the ZnSe/ZnS C/S QDs and ZCIS/ZnS C/S QDs. Warm white light was emitted from the fabricated white LEDs due to a combination of characteristic emission peaks of the ZnSe/ZnS C/S QDs and ZCIS/ZnS C/S QDs (Figure 7a inset). When we

investigated the luminous efficacy of the fabricated warm white LEDs, we determined it was 3.7 lmW^{-1}. Although this is not a high value, the luminous efficacy is affected by the efficiency of the nUV LED chip and coated QDs, etc. The luminous efficacy of white LEDs can be increased by using a highly efficient nUV LED chip and by enhancing the efficiency of the coated QDs, a topic of further study. The CIE color coordinates, correlated color temperature, and color rendering index of the warm white LED were (0.4088, 0.3987), 3488 K and 61.2, respectively. The CIE chromaticity diagram shows that the chromaticity point of the white LEDs was located in the 'warm' white region, which was close to the standard illuminant B (T_c = 4870 K) (Figure 7b) [37].

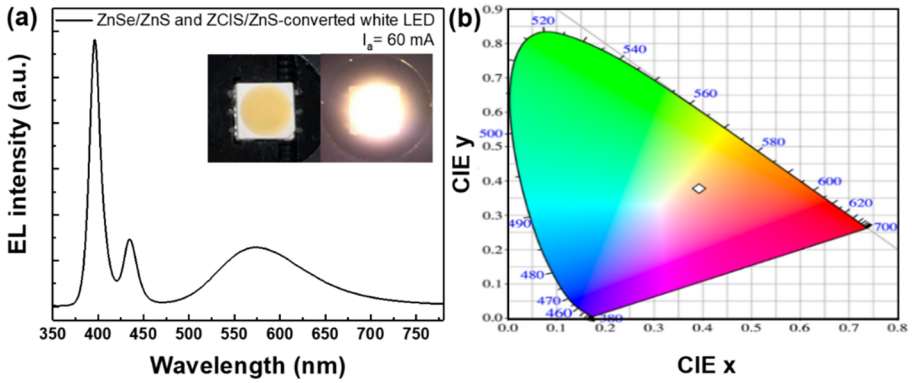

Figure 7. (**a**) EL spectra and (**b**) CIE color coordinates of the blue-emitting ZnSe/ZnS and yellow-emitting ZCIS/ZnS QD-converted warm white LEDs under an applied current of 60 mA. The inset shows photographs of the ZnSe/ZnS and ZCIS/ZnS QD-converted warm white LEDs (left) without and (right) with applied current.

4. Conclusions

In this study, eco-friendly, cadmium-free, blue-emitting ZnSe C QDs were successfully synthesized without phosphine precursors. The blue-emitting ZnSe C QDs were synthesized using a zinc-precursor injection method in a phosphine-free organic solvent at high temperature. The surfaces of the as-synthesized ZnSe C QDs were passivated with ZnS to reduce surface defects and increase confinement of the exciton for a higher PL QY. The ZnS shell was also formed on the ZnSe core without phosphine precursors. The C/S structure of the ZnSe/ZnS QDs was confirmed by XRD. The main XRD peaks of the ZnSe at 27.2°, 45.3°, and 53.5° were shifted to higher angles due to the ZnS shell, which caused lattice compression and confirmed the formation of the C/S structure. After the formation of the ZnS shell, the PL QY of the ZnSe increased from 19.4% to 37.4% and the ZnSe/ZnS C/S QDs emitted deep-blue light peaking at 425 nm. By utilizing the ZnSe/ZnS C/S QDs, nUV LED-pumped blue LEDs and warm white LEDs were fabricated. The white LEDs fabricated by coating the blue-emitting ZnSe/ZnS C/S QDs and the yellow-emitting ZCIS/ZnS C/S QDs on the nUV LED chip showed warm white light. These results indicate that the ZnSe/ZnS C/S QDs have good potential for white LED-based lighting applications.

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