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Abstract

We report the fabrication of efficient white light-emitting diodes (WLEDs) based on Cu : ZnInS/ZnS core/shell quantum dots (QDs) with super large Stokes shifts. The composition-controllable Cu : ZnInS/ZnS QDs with a tunable emission from deep red to green were prepared by a one-pot noninjection synthetic approach. The high performance Cu : ZnInS QD-WLEDs with the colour rendering index up to 96, luminous efficacy of 70–78 lm W−1, and colour temperature of 3800–5760 K were successfully fabricated by integration of red and green Cu-doped QDs. Negligible energy transfer between Cu-doped QDs was clearly found by measuring the photoluminescence lifetimes of the QDs, consistent with the small spectral overlap between QD emission and absorption. The experimental results indicated low toxic Cu : ZnInS/ZnS QDs could be suitable for solid state lighting.

Keywords: quantum dots, nanocrystals, Cu-doped quantum dots, white light-emitting diodes, energy transfer

1. Introduction

Energy-efficient lighting has offered a promising option for energy saving because artificial lighting globally consumes about 20% of the total electrical energy in the world [1]. Environmentally friendly white light-emitting diodes (WLEDs) with higher efficiencies, longer lifetimes, and fast response times are considered as promising light sources to replace the traditional ones such as incandescent or fluorescent lamps [2–6]. Currently conventional WLEDs have been fabricated by integrating down-converting phosphors with blue InGaN/GaN LEDs. However, the most popular commercial phosphors (Y3Al5O12 : Ce3+) show a deficient emission in the red spectral region and a serious scattering effect, which limit the colour rendering index (CRI) and luminescent efficiency of the WLEDs [7–8]. Therefore, it is necessary to find novel materials for fabricating high colour rendering WLEDs with high efficiency.

Semiconductor quantum dots (QDs) as potential converters for WLEDs exhibit size-tunable emissions, high photoluminescence quantum yields (PL QYs), low scattering and good colour saturation, compared to traditional phosphors [9–14]. The QD-WLEDs have been successfully demonstrated by employing the combination of red and green light-
emitting CdSe QDs on blue InGaN/GaN LEDs [15–19]. The CdSe QD-WLEDs were produced for display backlighting and they showed luminous efficacy of 41 lm W\(^{-1}\) and colour reproducibility of 100% compared to the National Television Systems Committee colour space [15]. However, the toxicity of the cadmium element and the significant self-absorption and energy transfer in closely packed QDs with small Stokes shifts potentially hinders their ultimate research transformation and commercialization [14, 15, 20]. Recently, low toxic CuInS\(_2\)-based QDs with large Stokes shifts and high PL QYs (60%–70%) were used for fabricating high colour rendering WLEDs [21]. The devices integrating green and red emitting CuInS\(_2\)-based QDs with blue chips showed a CRI of 95 and luminous efficacy of \(\sim 69\) lm W\(^{-1}\) [21]. Despite all, the spectral overlap between the green CuInS\(_2\)-based QD emission and red QD absorption in the WLEDs might result in significant energy transfer and re-absorption processes [20, 22], influencing the optoelectronic performances of the devices [23, 24]. Thus, it is desirable to develop the ideal QDs with low toxicity, high PL QY, and enough large Stokes shift for WLEDs.

Transition metal ions (such as Mn and Cu) doped QDs exhibited good thermal and chemical stability [25], and super large Stokes shift [14, 26, 27]. Mn-doped QDs with a yellow-orange emission and a PL QY of \(\sim 68\%\) were reported in our previous works [25, 28]. However, the Mn-doped QDs with the emission wavelength of (580–600 nm) are not suitable for fabrication of high colour rendering WLED. It is well known that the emission wavelength of Cu-doped QDs can be varied for WLEDs with low toxicity, high PL QY, and enough large Stokes shift for WLEDs. 

2. Experimental section

2.1. Materials

Zinc acetate (Zn(OAc)\(_2\), 99.99%), copper acetate (Cu(OAc)\(_2\), 99.99%), indium acetate (In(OAc)\(_3\), 99.99%), sulfur powder (S, 99.99%), dodecanethiol (DDT, 99%), oleyamine (OAm, 97%), 1-octadecene (ODE, 90%), were purchased from Aldrich. All chemicals were used without further purification.

2.2. Synthesis of Cu : ZnInS and Cu : ZnInS/ZnS QDs

The Cu : ZnInS and Cu : ZnInS/ZnS QDs used in this experiment were synthesized via a one-pot noninjection synthetic approach similar to our previous works [30]. In a typical procedure, Cu(OAc)\(_2\) (0.02 mmol), Zn(OAc)\(_2\) (0.2 mmol), In(OAc)\(_3\) (0.2 mmol), sulfur powder (1.6 mmol) together with 4.0 mL of DDT, and 6.0 mL of OAm were loaded in a 50 mL three-neck flask clamped in a heating mantle. The mixture was heated to 220 °C with a heating rate of 15 °C min\(^{-1}\) under argon flow and kept at this temperature for 10 min to allow the growth of Cu : ZnInS cores. Then the reaction mixture was allowed to cool to 100 °C, the Zn precursor (obtained by dissolving 0.4 mmol of Zn(OAc)\(_2\) in 0.2 mL of OAm and 0.8 mL of ODE) was then introduced into the reaction mixture. Following this, the system temperature was raised to 240 °C with a heating rate of 15 °C min\(^{-1}\) and kept at this temperature for 20 min to allow the overgrowth of ZnS shell around the preformed Cu : ZnInS cores. To obtain Cu : ZnInS cores with different Zn/In ratios, the Zn/In precursor ratio was varied while the gross amount of Zn and In precursors and all other variables were remained constant.

2.3. Device fabrication

Cu : ZnInS/ZnS QDs (0.1–0.2 g) in chloroform (3 mL) was blended with 0.3 g of thermally curable silicone resin under vigorous stirring. Then this QD-resin mixture was placed on hot plate at 50 °C for 1 h to evaporate the chloroform. Subsequently, 0.15 g of a hardener was added to the above QD-resin re-mixture. The composite was put into a vacuum oven for 30 min at 50 °C to eliminate any air bubbles. The 450 nm emitting InGaN-based blue LED (device efficacy of about 30 lm W\(^{-1}\) at 20 mA, Sanan Optoelectronics, China) without an silicone package was used to fabricate the QD-based LEDs. The QD paste was dispensed on a blue LED mold and then thermally cured by a two-step process of 100 °C for 30 min, followed by 120 °C for 1 h. For comparison, the fabrication of the WLEDs based on CdSe/ZnS QDs (Najing
Technology Corporation Limited, L51 and L55, PL QYs over 40%) was performed, which was similar to the method for Cu : ZnInS/ZnS QD-WLEDs. The weight ratio of green CdSe/ZnS QDs to the red ones was 7/1.

2.4. Characterization

The absorption spectra were recorded by a UV-3101PC UV-vis-NIR scanning spectrophotometer (Shimadzu). The PL spectra were recorded by a Hitachi F-7000 spectrophotometer. The time-resolved PL spectra were measured by an FL920 fluorescence lifetime spectrometer (Edinburgh Instruments). The excitation source was a hydrogen flash lamp (nF900) with a pulse width of 1.5 ns. The size and shape of the QDs were measured by a Tecnai G2 transmission electron microscope (TEM) operated at 200 kV. X-ray diffraction (XRD) patterns of the QDs were collected by a Bruker XRD spectrometer with a Cu Kα line of 0.15418 nm at a scanning step of 0.02°. The PL QYs of QDs were estimated by comparing the integrated emission of the QD samples in solution with that of standard dye solutions with identical optical density. The optical properties of QD-WLEDs were measured by an USB4000 Ocean Optics spectrometer with an integrating sphere. All measurements were carried out at room temperature.

3. Results and discussion

Figure 1 shows UV-visible absorption of Cu : ZnInS/ZnS core/shell QDs and the corresponding normalized PL spectra under excitation at 450 nm. The absorption spectra become steep around 350 nm due to the ZnS shell coating [21]. No distinct excitonic absorption peak is observed, which could be attributed to their irregular elemental distribution and/or intra band gap states [35]. Both the absorption onset and peak wavelength of the emission are red-shifted with increasing In/Zn precursor ratio in the cores from 1/1 to 8/1. The red shift could be explained by the change in the band gap of the alloy structures with the different ratio of ZnS (bandgap of 3.7 eV) and In2S3 (bandgap of 2.1 eV), since the emission in Cu-doped QDs derives from the radiative recombination of the electron in the conduction band of host material and the hole in Cu T2 state [29–32]. Therefore, the Cu : ZnInS QDs exhibit a super large Stokes-shift of about 140–180 nm, compared with that of undoped CdSe QDs about 20 nm [15]. The Cu : ZnInS/ZnS QDs exhibit an emission peak at 525, 560, 590, 630, and 670 nm, called as G-, Y-, O-, R-, and Dr-QDs, respectively, covering the green to red region of the visible spectrum, and they possess the PL QYs of 40–60%. The full width at half maximum of the Cu : ZnInS QD emissions are approximately 90–130 nm, which might be beneficial in solid state lighting due to the large spectral coverage [24].

Structural characterization for the typical green and red emissive Cu-doped QDs was carried out by means of TEM and XRD, which were shown in figure 2. The TEM images demonstrate that the G- and R-QDs are near-spherical in shape and monodispersed. The average diameters of the G- and R-QDs were estimated to be 3.3 and 3.9 nm, respectively. The QDs exhibit clear lattice fringes in the high-resolution TEM images as shown in the inset of figures 2(a), (b), which suggests the highly crystalline nature. The wide-angle XRD patterns for the Cu-doped QDs show the characteristic peaks of the zinc blende (cubic) structure, similar to those reported before [30]. The Cu : ZnInS QDs with small sizes, tunable broad emissions, high PL QYs, and super large Stokes-shifts are promising for fabrication of WLEDs [2, 36].

For the fabrication of QD-based LEDs, Cu : ZnInS/ZnS QDs with green, yellow, orange, red, and deep red emissions were utilized as colour converters and combined with a blue (450 nm) emitting LED chip. The normalized electroluminescence (EL) spectra of Cu : ZnInS/ZnS QD-based LED devices are shown in figure 3(a). To evaluate the quality of the light emitted from Cu : ZnInS QD-based LEDs, several parameters, such as Commission Internationale de l’Eclairage (CIE) chromaticity coordinates, CRI, correlated colour temperature (CCT), and luminous efficacy need to be determined [2, 37]. As seen in figure 3(b), the CIE colour coordinates of Cu : ZnInS QD-based LEDs with various concentrations of QDs in the silicone resin can cover the white light region. With increasing the concentration of QDs, the CIE coordinates move towards the white light region.
coordinates of the LEDs using the same QDs show a nearly linear increase trend. The slope of these lines monotonously decreases from 2.23 to 0.61 as the QD emission wavelength changes from green to deep red. These lines could guide us for the WLED design and provide the advantages for colour displays.

The device parameters for typical LEDs based on G-, Y-, O-, R-, and Dr-Cu:ZnInS/ZnS QDs operated at 20 mA are listed in table 1. The luminous efficiencies of the LEDs with green-, yellow-, orange-, red-, and deep red-emitting QDs were 87.2, 76.9, 53.5, 34.6, and 12.1 lm W\(^{-1}\), respectively. The superiority in luminous efficacy of a green doped QD-based LED relative to the red doped QD-based one mainly originates from the variety of colour sensitivity [37]. The CCT values were determined in a relatively wide range of 8110–1809 K, which shows a decrease with changing the QD emission wavelength from green to red. The CRI values for the WLEDs based on G- or Y- Cu:ZnInS QDs were in the range of 71–74. This indicates that the Cu:ZnInS QDs are good colour converters for the next generation of white solid state lighting.

The blue chip-to-QD light conversion efficiency was calculated from the integrated spectral ratio of the QD emission intensity to the absorbed source light intensity, based on the reduction of the original blue LED spectrum [38]. The light conversion efficiency of Cu:ZnInS QD-based LEDs and PL QYs of the Cu-doped QDs in solution are shown in figure 4(a). The light conversion efficiency deceased from 57% to 39% for different colour Cu:ZnInS QD-based LEDs, which showed a similar trend as the light-emitting efficiencies of the QDs in solutions. As we know that both the strong energy transfer/self-absorption and the surface defects of QDs generated through the LED fabrication (such as high temperatures for silicone encapsulation) have a detrimental impact on the efficiencies of the LEDs [15, 20, 39]. The degree of energy transfer and self-absorption in the QD ensembles significantly depends on the spectral overlap between absorption and emission spectra [40]. The absorption and emission spectra for Cu-doped QDs and undoped QDs, such as CdSe, were shown in supplementary figure S1, a remarkably enlarged Stokes shift for the doped QDs (140–180 nm) was observed, compared to the undoped ones (12 nm). To quantify the spectral overlap, we calculated the overlap integral \( J \) with the equation [40]:

\[
J = \int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda,
\]

where \( F_D(\lambda) \) is normalized donor emission spectrum, and \( \varepsilon_A(\lambda) \) is the acceptor molar extinction coefficient. The overlap integral \( J \) value for CdSe QDs is \( 3.434 \times 10^{16} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4 \), while that for G-, Y-, O-, R-, and Dr-Cu:ZnInS QDs is \( 2.545 \times 10^{14}, 1.648 \times 10^{14}, 4.463 \times 10^{14}, 2.808 \times 10^{14}, \) and \( 2.362 \times 10^{14} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4 \), respectively. The overlap integrals for the Cu-doped QDs are two orders of magnitude lower than that of the undoped QDs, owing to the huge Stokes shift in the doped QDs [41]. This significant difference suggests that energy transfer and self-absorption between the Cu:ZnInS QDs could be negligible. In addition, the luminescence decay curves of the G-Cu:ZnInS QDs in chloroform solution and in silicone resin (thermally cured as the LED fabrication) were measured by time-resolved PL spectroscopy, respectively, to investigate whether an additional nonradiative de-excitation channel of QDs occurred during the LED fabrication, as seen in figure 4(b). We analyzed the PL decays by a bi-exponential function with two time components (\( \tau_1 \) and weights (\( A_i \)). The amplitude-weighted lifetimes were obtained by a relation \( \tau_{\text{av}} = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2) \). The lifetimes of the G-Cu:ZnInS QDs in solution and silicone resin were estimated to be 432 and 419 ns, respectively, basically the same. This result confirmed that almost no additional nonradiative channels (e.g. energy transfer or thermally induced surface traps) occurred in the LEDs. This demonstrates that the energy transfer and thermally curing induced luminous efficacy reduction is not significant in Cu:ZnInS QD-based LEDs, which makes the Cu-doped QDs ideal emitters for WLEDs. In addition, the emission in Cu-doped QDs is considered to come from the recombination of the electron in the conduction band with the hole in Cu T\(_2\) state. Due to the incorporation of an additional energy state by Cu-doping, the excited-state lifetime of the dopant emission is
longer than the excitonic emission of QDs, reaching up to several microseconds or hundred-nanoseconds [42]. Further, the EL spectra of the Cu-doped QDs exhibit a small red-shifts (around 10 nm) in comparison to the PL spectra of the corresponding QDs in solution, which may be caused by the different dielectric constant of the QD-surrounding medium (chloroform versus silicone resin) [13, 43]. It is noted that the red-shifts for Cu : ZnInS QDs are extremely smaller than that for alloyed CuInS2-ZnS QDs (about 75 nm) [21], possibly because strong energy transfer between CuInS2-ZnS QDs might result in a large red-shift of the emission [21]. Therefore, the experimental results indicate that the Cu-doped ZnInS QDs are ideal candidates for fabricating high efficiency WLED [2].

Although QD-WLEDs can be fabricated by using a single type of Cu : ZnInS/ZnS QDs, the colour rendering property (CRI of 59–74) does not still satisfy the requirements for specific lighting applications (e.g. indoor illumination, CRI > 80) [2, 19]. The combination of green and red emitting QDs can provide an effective way to improve the lighting quality of WLEDs. In general, strong energy transfer and re-absorption between green and red undoped QDs such as CdSe nanocrystals have a detrimental impact on the luminous efficacy of WLEDs with increasing the QD packing density or
loading fraction [15, 35]. Many undoped QD-based WLEDs suffered from the embarrassing situation [13, 44, 45]. Moreover, QDs with shorter wavelength need a high content ratio to the longer wavelength ones to obtain high CRI values due to the energy transfer. Therefore, the energy transfer between G- and R-Cu : ZnInS/ZnS QDs was specially investigated by time-resolved PL spectroscopy. The energy transfer process acting as an additional nonradiative de-excitation channel for the donor can be described by the following expression 1/

\[ \frac{1}{\tau_{\text{donor-acceptor}}} = \frac{1}{\tau_{\text{donor}}} + k_{\text{ET}} \]

where \( \tau_{\text{donor-acceptor}} \) and \( \tau_{\text{donor}} \) are the PL lifetimes of G-Cu : ZnInS QDs donor in green and red QD blend and green QD neat resin films, respectively, and \( k_{\text{ET}} \) is the energy transfer rate [40]. The luminescence decay curves of the G-Cu : ZnInS QDs in G- and R-Cu : ZnInS QD blend films (weight ratio is 1/1) were measured, as seen in figure 4(b), similar to that in G-QD neat resin film. The PL lifetime of G-Cu : ZnInS QDs in green and red QD blend resin films (403 ns) is nearly the same as that in green QD neat resin film (419 ns). The corresponding energy transfer efficiency is only 4%, obtained by an expression \( 1 - \frac{\tau_{\text{donor-acceptor}}}{\tau_{\text{donor}}} \). This indicates that energy transfer between G- and R-Cu : ZnInS/ZnS QDs can be negligible, making us to use the green and red Cu : ZnInS QDs together for the WLEDs without a significant reduction in luminous efficacy.

In multiphase emitters-based WLEDs, the intensity ratio of the emissions with different colours has a great impact on the quality of devices. The performance parameters of the QD-WLEDs fabricated with the QD blend (G- and R-Cu : ZnInS with different weight ratio) and blue LED chips and operated at 20 mA are summarized in table 2. The typical EL spectra of the WLED with G- and R-Cu : ZnInS weight ratio of 1.4/1 at different forward current from 5 to 100 mA are shown in figure 5. Three distinct peaks at 450, 540, and 620 nm, corresponding to blue chip, green and red Cu-doped QDs, respectively, are clearly observed in the broad EL spectrum from 430 to 800 nm, as seen in figure 5(a). Owing to such a spectral extension, the G- and R-Cu : ZnInS QD blend-based WLEDs exhibit an improved CRI value of 94–96 as listed in table 2, and the corresponding luminous efficiencies of above 70 lm W\(^{-1}\), which are better than those for R- and G-CdSe QD-based WLEDs in the literature (luminous efficacy of 41 lm W\(^{-1}\)) [15]. Besides, for fair comparison, the CdSe/ZnS QD-WLEDs were fabricated with the same type of blue LED as used in the Cu : ZnInS QD-WLEDs. The corresponding EL spectrum is shown in supplementary figure S2, the luminous efficacy is 58 lm W\(^{-1}\), the CRI value is 84, the CCT is 5043 K, and the colour coordinate is (0.3421, 0.3298). It is found that, at the similar coordinates (0.34, 0.33) and CCT (about 5100 K), the luminous efficacy of Cu : ZnInS QD-WLED (1.4/1) can reach 74.7 lm W\(^{-1}\), while the CdSe/ZnS system can only reach 58 lm W\(^{-1}\). Obviously, the improved efficacy could be accounted by high PL QYs of the Cu : ZnInS/ZnS QDs and negligible energy transfer between the doped QDs. Furthermore, the optimized WLEDs exhibit a tunable CCT between 3800 and 5760 K by finely tuning the ratio and amount of the G-Cu : ZnInS QDs to the red ones, as seen in table 2, which can provide warm enough CCT (<4000 K) with high enough CRI (>80) white light for indoor illumination applications [2, 19].

### Table 2. The CRI, luminous efficacy (LE), CCT, and CIE colour coordinates of the as-fabricated WLEDs based on G- and R-Cu : ZnInS/ZnS QD blends with different weight ratios (from 1.6/1 to 0.9/1) operated at 20 mA.

<table>
<thead>
<tr>
<th>G/R</th>
<th>CRI</th>
<th>LE  (lm W(^{-1}))</th>
<th>CCT (K)</th>
<th>CIE (x, y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6/1</td>
<td>94</td>
<td>78.3</td>
<td>5760</td>
<td>(0.3271, 0.3232)</td>
</tr>
<tr>
<td>1.4/1</td>
<td>95</td>
<td>74.7</td>
<td>5198</td>
<td>(0.3388, 0.3337)</td>
</tr>
<tr>
<td>1.2/1</td>
<td>96</td>
<td>72.5</td>
<td>4655</td>
<td>(0.3528, 0.3416)</td>
</tr>
<tr>
<td>1/1</td>
<td>96</td>
<td>71.2</td>
<td>4147</td>
<td>(0.3710, 0.3596)</td>
</tr>
<tr>
<td>0.9/1</td>
<td>96</td>
<td>70.5</td>
<td>3804</td>
<td>(0.3863, 0.3721)</td>
</tr>
</tbody>
</table>
of the WLED with G/R weight ratio of 1.4/1 are obtained to be (0.3388, 0.3337) under 20 mA forward bias current, which are close to the equi-energy white point (0.3333, 0.3333). The values exhibit little change under different forward bias currents, as seen in figure 5(b), indicating good colour stability of the output light of the WLED.

The detailed CRI values of R1-R9 and the general CRI of the WLED with sun light, a fluorescent lamp, and the WLED operated at 100 mA. Photographs of colourful candy are compared under the illumination with sun light (b), a fluorescent lamp (c), and a Cu : ZnInS QD-based WLED operated at 100 mA.

![Figure 6](image_url)

Figure 6. (a) CRI of the fluorescent lamp (Panasonic YZ18RR6500K) and G- and R-Cu : ZnInS QD-WLED operated at 100 mA. Photographs of colourful candy are compared under the illumination with sun light (b), a fluorescent lamp (c), and a Cu : ZnInS QD-based WLED operated at 100 mA.

4. Conclusions

In summary, we have fabricated high performance Cu : ZnInS/ZnS QD-WLEDs for the next generation solid state lighting. Highly luminescent Cu : ZnInS QDs with PL QYs of 40–60% and tunable emissions from green to deep red were obtained by effectively controlling the component of the QDs. The optimized warm WLEDs based on G- and R-Cu : ZnInS/ZnS core/shell QDs and blue LED chips exhibited high CRI up to 96, luminous efficacy of 70–78 lm W\(^{-1}\), CCT of 3800–5760 K, and CIE colour coordinates of (0.3388, 0.3337), which are the best values currently reported for QD-WLEDs. No significant change in PL lifetimes of the G-Cu : ZnInS/ZnS QDs in G- and R-QD blend films was observed, compared with those in solution. This indicated that the energy transfer between G- and R-Cu : ZnInS QDs in WLEDs could be negligible. This resulted in a higher luminous efficacy in doped QD-WLEDs than the undoped QD devices. These experimental results suggest that low toxic Cu : ZnInS QDs are promising colour converting materials for fabricating high colour rendering WLEDs with high efficiency.

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