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Research Article

ZnCuInS/ZnSe/ZnS Quantum Dot-Based Downconversion Light-Emitting Diodes and Their Thermal Effect

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The quantum dot-based light-emitting diodes (QD-LEDs) were fabricated using blue GaN chips and red-, yellow-, and green-emitting ZnCuInS/ZnSe/ZnS QDs. The power efficiencies were measured as 14.0 lm/W for red, 47.1 lm/W for yellow, and 62.4 lm/W for green LEDs at 2.6 V. The temperature effect of ZnCuInS/ZnSe/ZnS QDs on these LEDs was investigated using CIE chromaticity coordinates, spectral wavelength, full width at half maximum (FWHM), and power efficiency (PE). The thermal quenching induced by the increased surface temperature of the device was confirmed to be one of the important factors to decrease power efficiencies while the CIE chromaticity coordinates changed little due to the low emission temperature coefficients of 0.022, 0.050, and 0.068 nm/°C for red-, yellow-, and green-emitting ZnCuInS/ZnSe/ZnS QDs. These indicate that ZnCuInS/ZnSe/ZnS QDs are more suitable for downconversion LEDs compared to CdSe QDs.

1. Introduction

Semiconductor colloidal quantum dots (QDs) exhibit unique properties of tunable band gap, broad absorption, and high photoluminescence (PL) quantum yield (QY), making them highly attractive materials for wide applications, including photovoltaics [1, 2], light-emitting diodes (LEDs) [3–9], and bioimaging [10, 11]. Achermann et al. reported the mechanism and viability of CdSe QDs-based color conversion white LEDs (WLEDs) [12], and CdSe or its derivative QDs have been most widely used as phosphors for LED fabrication by adopting one [13–15] or multiple types [16–19] of QD emitters, depending on the desired emission color. It has been demonstrated that the downconversion WLED devices integrated with red-emissive CdSe/ZnS [20–23], CdSe/CdS/CdZnS/ZnS [24], CdSe/ZnSe [25], or CdS:Cu/ZnS [26] QDs show improved color rendering metrics.

However, the toxicity of Cd element makes its use undesirable in terms of human and environmental impacts, limiting the practical application of Cd-based LEDs. The $CuInS_2$ based QDs have been investigated as low toxic alternatives. The emission color of $CuInS_2$ QDs can be tuned from visible to the near-infrared (near-IR), making them relevant for applications in lighting and displays. The band gap of $CuInS_2$ QDs is tunable mainly through changing their particle size [27–29], composition [30], or alloying with ZnS [31–33]. There are many kinds of methods to enhance the PL QY of $CuInS_2$ QDs. Among them, the methods of doping Zn ion [31] or using dodecanethiol as both a sulfur source and a stabilizing ligand [28] have been applied widely. In 2011, Zhang et al. and Chung et al. published

their results on highly luminescent ZnCuInS QDs [32, 34]. For LED applications, Song and Yang developed a WLED consisting of yellow-emitting $CuInS_2$/ZnS QDs pumped by an InGaN blue LED [35]. They reported a high luminous efficiency of 63.4 lm/W. Chung et al. used ZnCuInS QDs and their LEDs exhibited a color rendering index (CRI) of 84.1 with a color temperature of 4256 K [6]. Chen et al. fabricated a WLED by combining red-emissive $CuInS_2$ QDs with the commercial yellow-emissive YAG:Ce and green-emissive Eu^{2+} doped silicate phosphors [36]. Their warm WLED had a CRI of 92 with luminous efficiency of 45~60 lm/W and color temperature of 4000 K.

In this work, we adopted colloidal ZnCuInS/ZnSe/ZnS QDs as the environmentally benign and nontoxic phosphor. Red-, yellow-, and green-emitting ZnCuInS/ZnSe/ZnS QDs were synthesized and deposited on GaN blue LED chips. The temperature-dependent PL spectra of QDs showed the corresponding changes of band gap, intensity, and FWHM (full width at half maximum) [37, 38]. Therefore, the thermal effect was investigated according to the evolutions of power efficiencies (PE), FWHM, and peak wavelength.

2. Experimental Section

2.1. Chemicals. Indium (III) acetate ($In(Ac)_3$, 99.99%), selenium powder (Se, 100 mesh), copper (I) acetate (99.99%), zinc acetate ($Zn(Ac)_2$, 99.99%), oleic acid (OA, 90%), and 1-octadecene (ODE, 90%) were purchased from Alfa Aesar. Oleylamine (97%), sulfur powder (S, 99.99%), dodecylthiol (99.9%), acetone, methanol, hexane, and toluene were purchased from Sigma-Aldrich. Tributylphosphine (TBP, 95%) and diethyldithiocarbamic acid zinc (DECZn, 98%) were obtained from Aladdin. All chemicals were used directly without further treatment.

2.2. Synthesis. Several solutions were prepared before the QD synthesis. 0.181 g DECZn was mixed with 6 mL TBP and 24 mL ODE under N_2 and was heated to 70°C for 30 min until a colorless solution was obtained as DECZn/TBP/ODE solution. 0.078 g Se powder was dissolved into 10 mL TBP at room temperature as Se/TBP solution. 0.1003 g ZnO and 2.073 g OA were mixed with 10 mL ODE and loaded into a 25 mL three-necked flask; the mixture was degassed under N_2 for 10 min and was heated to 200°C until a colorless solution was formed as Zn solution.

ZnCuInS core QDs were synthesized following the method by Zhang et al. [32] In a typical synthesis of ZnCuInS core QDs, 0.0528 g zinc acetate (0.3 mmol), 0.0292 g indium acetate (0.1 mmol), 0.0190 g copper (I) acetate (0.1 mmol), 1-dodecanethiol (2 mmol), and oleic acid (0.6 mmol) were mixed with 4 mL ODE in a three-neck flask and degassed under N_2 for 10 min. The mixture was heated to 210°C until the powders dissolved completely. The sulfur solution (0.3 mmol S dissolved in 0.5 mL oleylamine) was quickly injected into the solution. After maintaining the temperatures (210, 180, and 150°C for red, yellow, and green QDs, resp.) for 10 min, the mixture was heated to 230°C and maintained for 5 min and then cooled to room temperature. The core QDs were thus achieved.

Then, ZnSe/ZnS shell/shell were synthesized as follows: 2 mL Se/TBP and 2 mL ZnO/OA/ODE solution were added drop by drop into the above solution. After 10 min, another 2 mL Se/TBP and 2 mL ZnO/OA/ODE solution were added dropwise. 10 min later, 3 mL DECZn/TBP/ODE was added into the solution. Then, the temperature was maintained at 150°C for 2 hours. The solution was mixed with an equal volume of hexane and twice the volume of methanol to extract byproducts. After that, the QDs were redispersed in hexane and were precipitated by twice the volume of methanol and an equal volume of acetone to get pure ZnCuInS/ZnSe/ZnS QD powders [39–41].

2.3. Downconversion LEDs. ZnCuInS/ZnSe/ZnS QDs were dispersed into chloroform. A transparent epoxy was prepared by mixing EP-3400 A and EP-3400 B (Swancor Fine Chemical Co.) with a mass ratio of 1 : 1. Then, the QD solution was dropwise added into the epoxy. The mixture was well stirred until it became homogeneous. The QD/epoxy mixture was firstly heated at 40°C for 30 min in a vacuum chamber (2×10^3 Pa) to remove chloroform and bubbles in the mixture. The temperature was further gradually increased to 80°C and was kept at 80°C for 60 min. After that, the QD/epoxy liquid mixture was deposited on LED chips dropwise and then was heated at 120°C for 45 min in the vacuum chamber to solidify the QD/epoxy on the LED chips.

2.4. Characterization. Absorption spectra were measured on a Perkin-Elmer Lambda 950 UV-vis spectrophotometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS50B spectrophotometer. For temperature control measurements, the sample stage was placed on a heating plate which controlled the temperature of the sample in the process of measurement. The sample was heated at an aimed temperature for 20 min before measurements. Temperature of GaN chip was measured by an infrared (IR) thermal image camera (FLIR T250). Images of LEDs were recorded with a Canon EOS 600D camera. The electrical characterization of the devices was performed on a Keithley 2612B source meter. The PL QYs of the QDs were calculated by comparing their integrated emissions with that of rhodamine 6G dissolved in ethanol (QY of ~96% was adopted) at an identical optical density of ~0.05 with 450 nm excitation. Samples for TEM studies were prepared by placing a 4 μL toluene solution of QDs on ultrathin carbon-film-coated copper grids in glove box. The element molar ratio of QD cores was determined with a Thermo Fisher Scientific X Series 2 inductively coupled plasma-mass spectrometer (ICP-MS). Prior to the analysis, the sample was dissolved in a mixed solution of ultrapure nitric acid and ultrapure hydrochloric acid. And then the solution was diluted by deionized water.

3. Results and Discussion

The UV-vis absorption and PL spectra of the QDs in chloroform are given in Figure 1(a). The PL peak wavelengths of

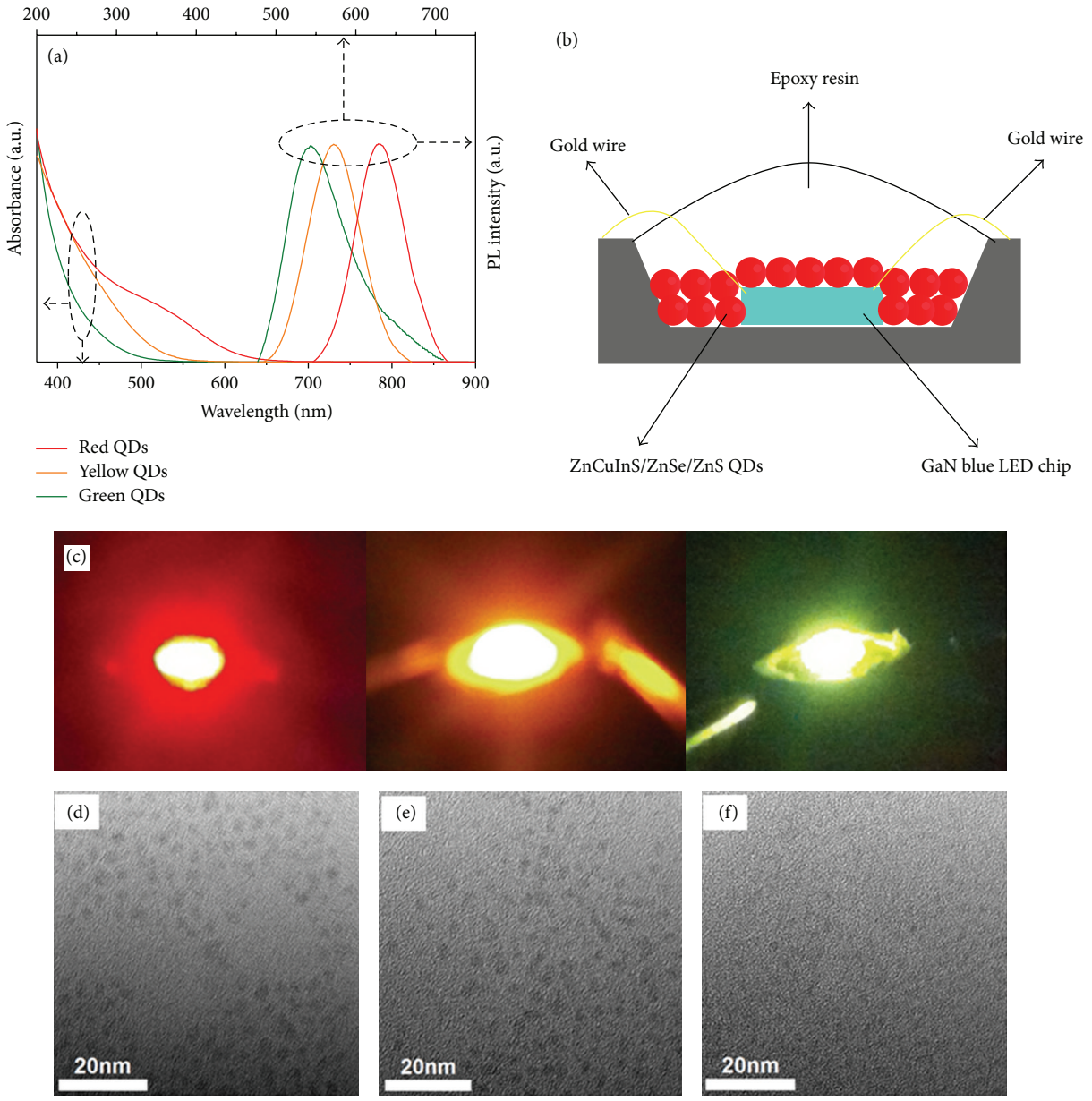

Figure 1: The absorption and PL spectra of ZnCuInS/ZnSe/ZnS QDs in chloroform (a); the device structure (b) and the emitting color photograph (c) of QD-LEDs; the TEM images of red (d), yellow (e), and green (f) ZnCuInS/ZnSe/ZnS QDs.

three ZnCuInS/ZnSe/ZnS QDs were 629.3 nm (PL QY 60%) for red, 572.7 nm (PL QY 59%) for yellow, and 543.5 nm (PL QY 65%) for green QDs, respectively. As shown in Figures 1(d)–1(f), the average sizes of three ZnCuInS/ZnSe/ZnS QDs were 3.4 nm for red, 2.8 nm for yellow, and 2.0 nm for green QDs, respectively. The elemental ratios of the red-, yellow-, and green-emitting ZnCuInS cores were Zn : Cu : In : S = ~3.0 : 1.0 : 1.3 : 9.3, ~3.1 : 1.0 : 1.4 : 9.2, and ~3.0 : 1.0 : 1.4 : 9.4, respectively, by ICP-MS. The elemental ratios are almost the same for three ZnCuInS/ZnSe/ZnS QDs. Therefore, the blue shifts of UV-vis absorption and PL spectra are attributed to the decreasing size. The QD-LEDs consisted of a GaN blue LED (HXGD-DZ-3w) and the QDs, as shown in Figure 1(b). In this device configuration, the 452.0 nm blue light from the GaN LED acted as the host, which could effectively excite the ZnCuInS/ZnSe/ZnS QDs. The QD phosphors converted the blue light into red, yellow, and green light. Photographs of red, yellow, and green emitting ZnCuInS/ZnSe/ZnS QD-LEDs operated at a bias of 2.6 V are shown in Figure 1(c).

Figure 2(a) shows the luminescence of red QD-LED at 2.6 V with different quantity (showing the added QD/epoxy liquid mixture volume) of ZnCuInS/ZnSe/ZnS QDs. Two emission bands of blue and red were contributed by GaN chip and ZnCuInS/ZnSe/ZnS QDs, respectively. The blue emission intensity of the underlying GaN LED chip decreased while the PL intensity of the QDs increased with the increasing amount of ZnCuInS/ZnSe/ZnS QDs. The blue emission disappeared when the QD layer was thick enough

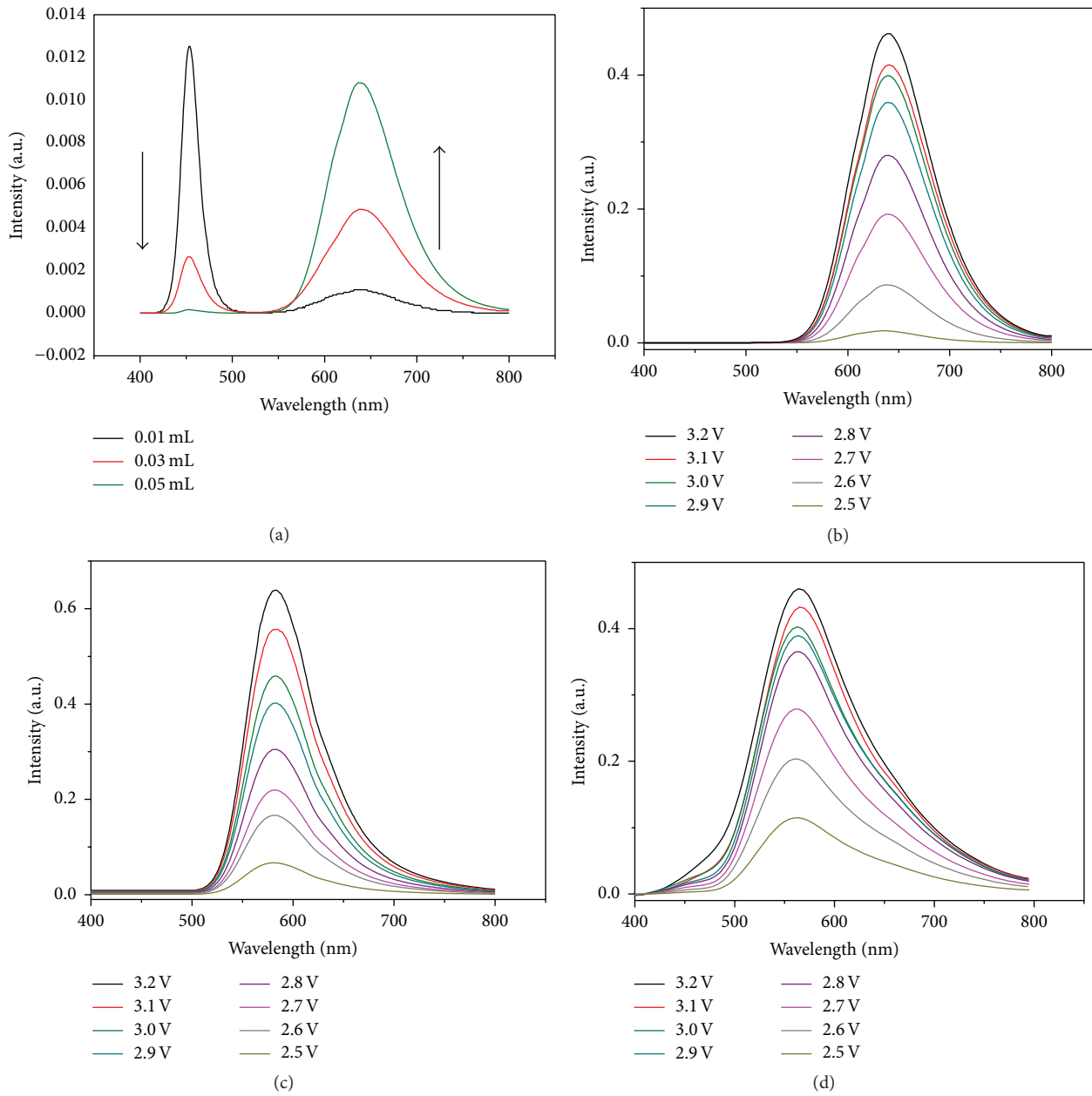

Figure 2: The evolution of LED spectra with the increase of QD quantity (a); the emission spectra of the as-fabricated LEDs under different voltage ((b) for red, (c) for yellow, and (d) for green LEDs).

to absorb the emission of GaN chip completely. Finally, the PL spectra of the as-fabricated three-color QD-LEDs under different voltages are shown in Figures 2(b), 2(c), and 2(d), in which the emission peaks of QDs are located at 639.3 nm, 581.4 nm, and 562.0 nm, respectively. The emission of the QD-LEDs had some red-shift compared to that of the original solution, which may be caused by the agglomeration of the QDs [20, 42–44].

The Commission Internationale de l'Eclairage (CIE) coordinates of the LED were calculated through the data of emission spectra; they were (0.660, 0.339), (0.655, 0.344) for red-, (0.521, 0.475), (0.524, 0.462) for yellow-, and (0.449, 0.519), (0.437, 0.502) for green-emitting QD-LEDs at 2.5 V and 3.2 V, respectively, as shown in Figure 3(a), indicating a good color stability. FWHM and the peak position for QD-LEDs under different voltage are shown in Figures 3(b), 3(c), and 3(d). Due to the defect-related emission of ZnCuInS/ZnSe/ZnS QDs, the red-shift and broaden of emission spectra with increasing voltage were little as shown in Figure 3.

FWHM of these LED emissions broadened from 84.7 to 90.3 nm for red, from 77.2 to 79.6 nm for yellow, and from

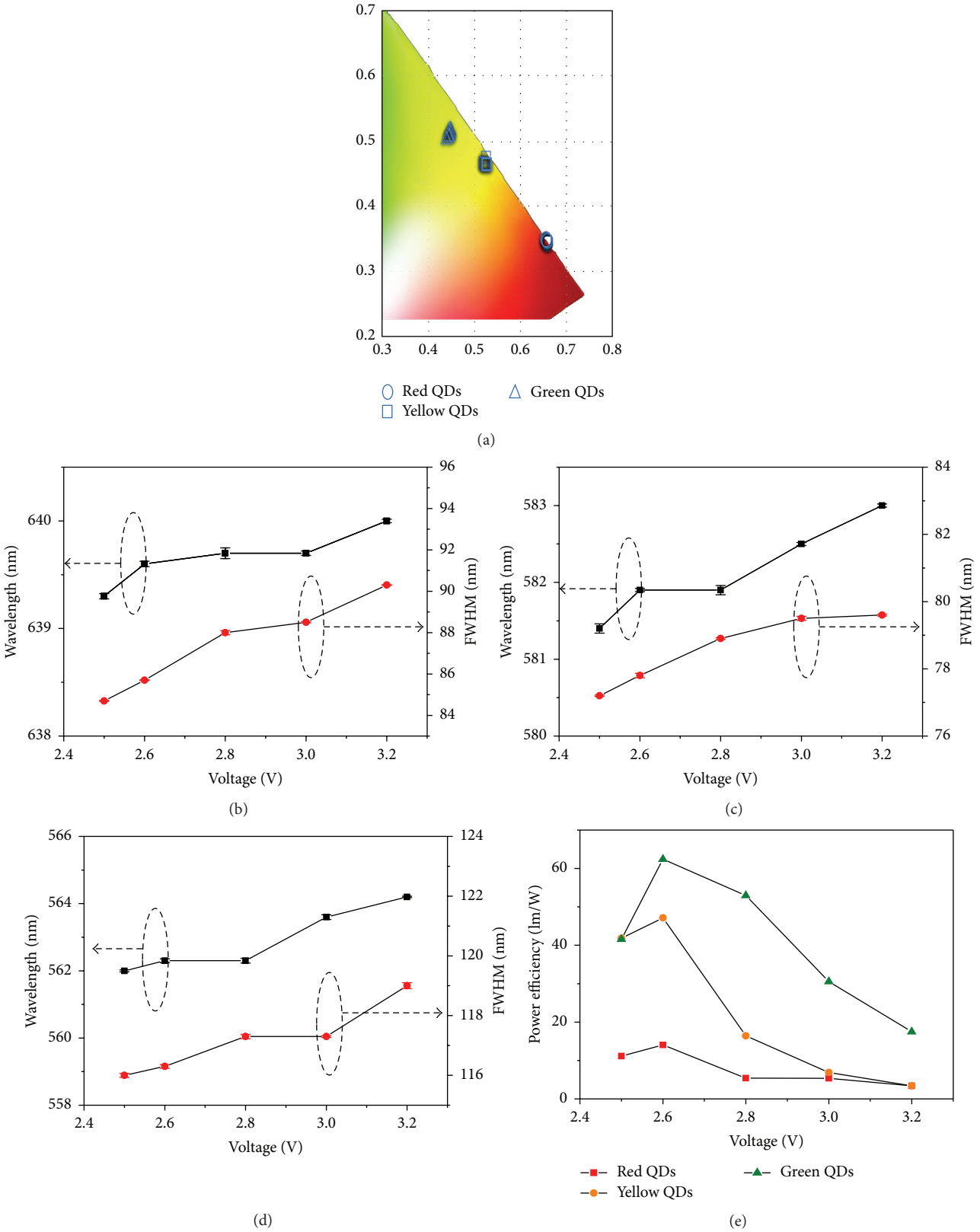

FIGURE 3: The CIE coordinates of LEDs under different voltage (a); FWHM and the peak position of LEDs under different voltage ((b) for red, (c) for yellow, and (d) for green LEDs); and power efficiency (PE) of LEDs at different voltage (e).

116 to 119 nm for green LEDs, respectively, with increased voltage. The spectra peaks of red-, yellow-, and green-emitting QD-LEDs at 2.5 V were 639.3, 581.4, and 562.0 nm, respectively, and showed slight red-shift with the increasing voltage. When the voltage increased from 2.6 V to 3.2 V, the PL spectra shifted to red from 639.6 to 640 nm for red-emitting QD-LEDs, from 581.9 to 583 nm for yellow-emitting QD-LEDs, and from 562.3 to 564.2 nm for green-emitting QD-LEDs. The peak position changed by only 0.7 nm, 1.6 nm, and 2.2 nm for red-, yellow-, and green-emitting QD-LEDs, respectively.

The power efficiencies (PE) of the as-fabricated QD-LEDs were calculated on based the following equation [45]:

$$\eta = \frac{F}{(IV)} = \frac{\pi SL}{(IV)} = \frac{\pi L}{(JV)}, \quad (1)$$

where η is the power efficiencies (PE, lm/W), S is the light-emitting area, F is the luminous flux (lm), I is the current (A), V is the voltage (V), π is the ratio of circumference to diameter (Pi), L is the luminance of LED (cd/m^2), and J is the current density (A/m^2). The PE increased with the increase of bias from 2.5 V to 2.6 V, corresponding to the maximum values of 14.0 lm/W, 47.1 lm/W, and 62.4 lm/W for red, yellow, and green LED at 2.6 V. In terms of the PE, the values are compatible with those of CdSe-based QD-LEDs [46].

The PE decreased when the bias further increased, which was caused by two factors: the PL QY of ZnCuInS/ZnSe/ZnS QDs and the GaN LED efficiency droop at high voltage. The drop of GaN or InGaN LED efficiency has been reported due to the effects induced by Auger recombination, density-activated defect recombination, and carrier leakage [47–49]. In order to deconvolute the voltage and thermal effects on device output, the emission spectra of QD films on the glass excited by GaN LEDs were record with increasing bias from 2.5 V to 3.2 V as shown in Figure 4(a). As a result, the emission peak and FWHM of QD films were not affected by the increasing bias. Then, the thermal effect of the devices was investigated. The images of the temperature profiles of the surface of GaN chip were measured by a thermal infrared imager (Figures 4(b)–4(d)). The working temperature of device changed from 28.1 to 60.3°C with the bias increased from 2.5 to 3.2 V as shown in Figure 4(e). As we know, the heat is proportional to the square of the voltage. Therefore, the temperature increased slowly when the voltage was low but increased quickly when the voltage was high. As shown in Figure 4(e), the temperature increased with the increasing voltage. At low voltages, the change of PL QY of ZnCuInS/ZnSe/ZnS QDs was inconspicuous. But the PL QY decreased sharply at high voltages. This is because the PL spectra were temperature-dependent [37]. Therefore, the intensity of the emission spectra of QD-LEDs increased more at low voltages than that at high voltages. Correspondingly, the PE of QD-LEDs decreased with the increasing voltage when the voltage was higher than 2.6 V.

The temperature-dependent PL spectra of the ZnCuInS/ZnSe/ZnS QD films were collected by an optical fiber (the QD films were placed on a heating plate). The relative temperature-dependent peak intensity of ZnCuInS/ZnSe/ZnS QDs decreased to 69.6% at 40°C and to 41.6% at 60°C compared with the one at room temperature (Figure 4(f)). In order to understand the temperature-dependent PL and determine the activation energy for thermal quenching, the Arrhenius equation was employed to fit the thermal quenching data [50]:

$$I_{(T)} = \frac{I_0}{1 + c\exp(-E/kT)}, \quad (2)$$

where I_0 is the initial intensity, $I_{(T)}$ is the intensity at temperature T, c is a constant, E is the activation energy for thermal quenching, and k is the Boltzmann constant. The fitting curve is shown in the inset of Figure 4(f). As shown in Figure 4(e), the surface temperature of the GaN chip increased slowly at low voltages, but sharply at high voltages. Correspondingly, the PL QY of ZnCuInS/ZnSe/ZnS QDs was little affected at low voltages than that at high voltages. It is because the activation energy of ZnCuInS/ZnSe/ZnS QDs was enough to restrain the thermal motion. When the voltage increased from 2.5 V to 3.2 V, the energy of thermal motion of $(3/2)kT$ increased from 25.9 meV to 43 meV. The energy of 43 meV was close to the activation energy of 50 meV. Therefore, the activation energy was not enough to restrain the effect of thermal motion. As shown in Figure 2, the intensity of the emission spectra of QD-LEDs increased more at low voltages than that at high voltages. Therefore, the suitable activation energy for the material of downconversion was concerned with the voltage of working range of the LEDs. The activation energy of 50 meV was not enough to overcome the thermal effect. But the activation energy was higher than those of CdSe and CdTe QDs [51, 52], which makes a relatively higher thermal stability of these ZnCuInS/ZnSe/ZnS QDs [53–55].

Emission temperature coefficient, the peak shift divided by the temperature change, is used to quantify the thermal effect on PL peak positions. A red-shift of 5.5 nm (green emission) was observed in the PL spectra of ZnCuInS/ZnSe/ZnS QDs when the temperature increased from 20 to 100°C, corresponding to a temperature coefficient of 0.068 nm/°C as shown in Figure 4(f). The spectra peak of the green-emitting LEDs showed a red-shift of 2.2 nm when the voltage increased from 2.5 V to 3.2 V with the corresponding increasing temperature of 32.2°C, which was in good accordance with the temperature coefficient of ZnCuInS/ZnSe/ZnS QDs.

Compared to CdSe QDs, the temperature-dependent shift of the PL spectra of ZnCuInS/ZnSe/ZnS QDs is small. The temperature coefficients of 0.022 nm/°C and 0.050 nm/°C were found for red- and yellow-emitting LEDs, respectively; all were much lower than that of CdSe QDs (~0.1 nm/°C) [56, 57]. The low temperature coefficients might be attributed to the donor or acceptor-related recombination because the surface-related recombination, conduction to defect state recombination, and donor-acceptor pair (DAP) recombination were considered to coexist in ZnCuInS/ZnSe/ZnS QDs [37, 57, 58]. The PE values of the ZnCuInS/ZnSe/ZnS QD-LEDs are approximate to the CdSe QD-LEDs. For the toxicity, the ZnCuInS/ZnSe/ZnS QDs do not contain toxic Cd element. But for the color purity, the CdSe QD-LEDs are better than ZnCuInS/ZnSe/ZnS QD-LEDs, because their emissions

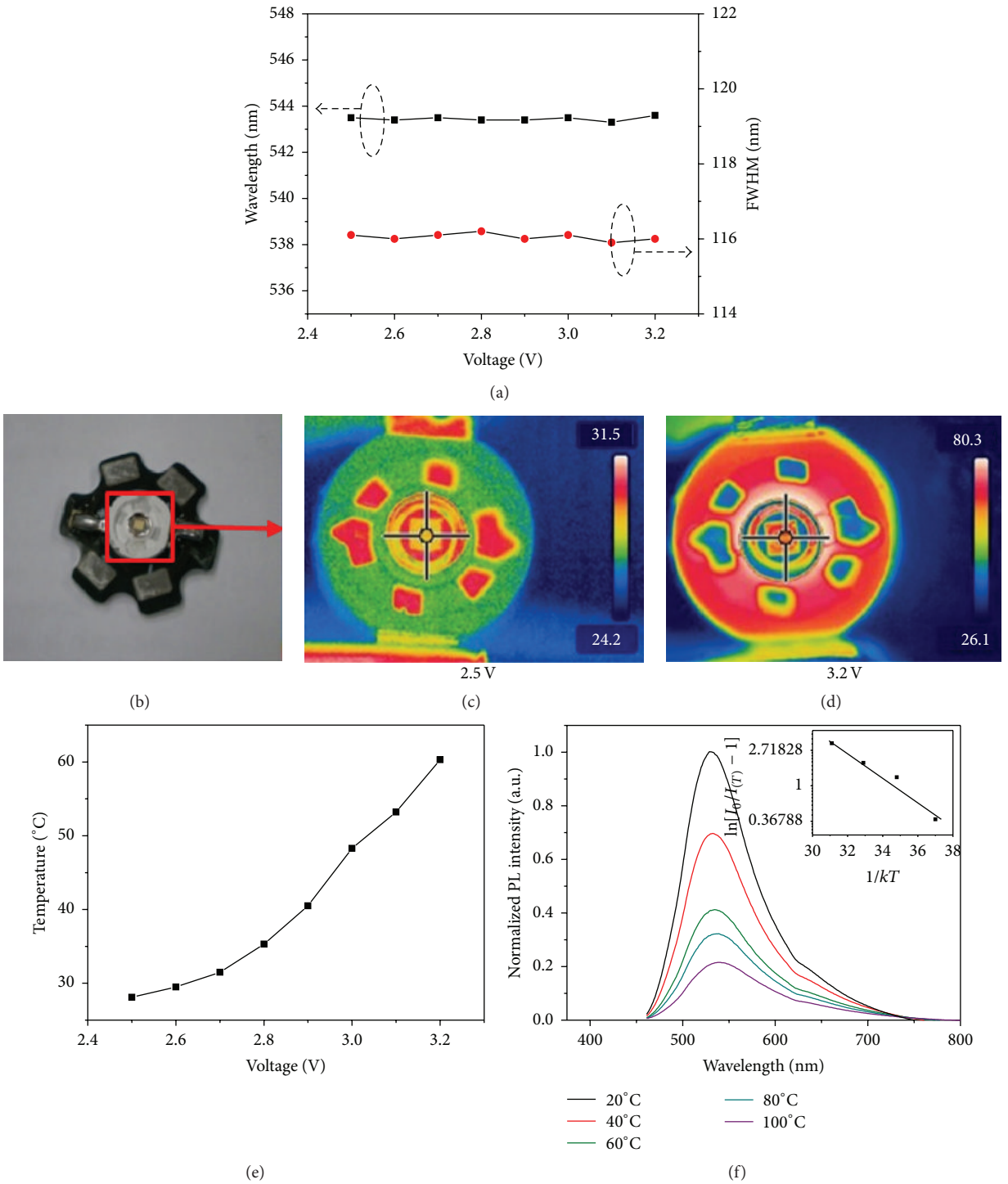

FIGURE 4: The peak position and FWHM of PL spectra of QD film excited by LED with different working bias (a); the images of GaN LED (b) and the thermal distribution of GaN LED at operating voltages of 2.5 and 3.2 V (c and d); the temperature of GaN chip at different voltages (e); temperature-dependent PL spectra (f) of green QDs in the range from 20 to 100°C (inset: the fitting curve according to (2)).

are narrower. This is still an active research topic in this group and many other labs. The color stability is an important specification for the monochromatic QD-LEDs and we found the temperature coefficients of ZnCuInS/ZnSe/ZnS QDs were small. Putting things together, ZnCuInS/ZnSe/ZnS QDs are more suitable for fabricating the QD-LEDs than CdSe QDs.

4. Conclusions

QD-based downconversion LEDs were fabricated using blue GaN chip and red-, yellow-, and green-emitting ZnCuInS/ZnSe/ZnS QDs. The CIE chromaticity coordinates were (0.658, 0.341)/(0.655, 0.344) for red, (0.517, 0.465)/(0.524, 0.462) for yellow, and (0.446, 0.518)/(0.437, 0.502) for green LEDs at 2.6/3.2 V with PE of 14.0/3.4, 47.1/3.4, and 62.4/17.5 lm/W, respectively. The thermal effect was investigated and small red-shift as well as a broadening of the emission peak was observed with increased temperature. The CIE chromaticity coordinates changed very little due to the low temperature coefficients of ZnCuInS/ZnSe/ZnS QDs which meant they were more suitable for downconversion LEDs compared to CdSe QDs. However, the decreasing PE caused by the increasing temperature of the GaN chip was still vital for the performance of QD-LEDs. Therefore, it is necessary to avoid higher working temperature of the GaN chips.

Conflict of Interests

All authors declare that this paper does not have any content with conflict of interests.

Acknowledgments

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