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The Application of $Zn_{0.8}Cd_{0.2}S$ Nanocrystals in White Light Emitting Diodes Devices

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In this study, the colloidal ternary semiconductor $Zn_{0.8}Cd_{0.2}S$ (ZnCdS) nanocrystals (NCs) with wide emission and high quantum yields (QYs) have been prepared and used as nanophosphors in white light emitting diodes (WLEDs). The optical properties of ZnCdS NCs-based WLEDs including Commission Internationale de l'Eclairage (CIE) chromaticity coordinates, correlated color temperature (CCT), color rendering index (CRI) and luminous efficiency can be adjusted by the various ZnCdS NCs, using different carbon chain lengths of alkenes as surface ligands, reaction time, NCs contents and encapsulation methods. The optimal conditions of CIE, CRI, CCT and luminous efficiency, and decay during stability test for ZnCdS NCs-based WLEDs are (0.32, 0.30), 82, 6811 K, 4.26 lm/W, and 0.036 lm/W-hr, respectively by the UV chip with only one type of ZnCdS NCs layer. The results have exhibited the potential application of ZnCdS NCs as nanophosphors in WLEDs.

Group II-VI semiconductor nanocrystals (NCs, also called quantum dots, QDs) have exhibited great potential applications in the fabrication of solid state white light emitting devices (WLEDs), owing to their novel optical properties such as tunable emission wavelengths and high quantum yields (QYs).[1-10] Because of the quantum confinement effect and the wide bandgap of these NCs, the narrow band emission can be tuned in the visible light range by controlling not only the particle sizes but also the compositions of the NCs.[11-15]

The semiconductor NCs-based WLEDs have been classified into three categories: (a) discrete color mixing, (b) color conversion and (c) direct white light generation.[16] The first approach for white light generation is to mix several colors of electroluminescent emissions (e.g., red, green, and blue).[17] However, this kind of devices suffers from the self-absorption caused by semiconductor NCs which result in the color instability and low efficiencies. The most common approach of WLEDs is color conversion which is usually based on blue LED chips and an appropriate blend of various colors of NCs. The Commission Internationale de l'Eclairage (CIE) chromaticity coordinates, correlated color temperature (CCT), and color rendering index (CRI) of WLEDs could be adjusted from (0.37, 0.25) to (0.24, 0.33), 14.69 to 71.07 and 2692 to 11171 K, respectively through varying size, compositions and concentration of NCs.[18,19] The WLEDs are successfully fabricated by blue chips and green and red emitting CdSe-ZnSe NCs which exhibit white light emission with a CIE chromaticity coordinates of (0.33, 0.33) and color rendering index of 91.[20] Recently, in order to eliminate the complex color mixing or conversion techniques for WLEDs, the utility of directly white light emitting NCs excited by the UV LED chips have been investigated.[16,21-23] The WLEDs assembled with the ultrasmall CdSe NCs have created white light with CIE coordinates of (0.33, 0.33) and a high CRI of 96.6.[24] Although the WLEDs based on direct white light generation have been fabricated successfully, the stability of optical properties and the luminous efficiency needs further improvements.

Previously, we have prepared highly effective ternary $Zn_{0.8}Cd_{0.2}S$ and $Zn_{0.5}Cd_{0.5}S$ NCs with white light emission.[25] NCs have been encapsulated with silicone resin to form WLEDs which may not only avoid the self-absorption from mixing several kinds of phosphors but also improve the CRI and luminous efficiency of the commercial WLEDs.[25,26] However, due to the low melting point of capping reagents and the curing is not complete for silicone-based resin, the performance of WLED is not good. Moreover, the correlation between QYs and the passivation effects from alkenes with different carbon chain lengths (decene (DE), tetradecene (TDE), or octadecene (ODE)) used as surface ligands for $Zn_{0.8}Cd_{0.2}S$ have been explored.[27] These white light emitting $Zn_{0.8}Cd_{0.2}S$ (named as ZnCdS for short) NCs with adjustable optical properties are used as nanophosphors in the fabrication of WLEDs based on direct white light generation in this study. Two kinds of encapsulating methods, convert and remote, are used to fabricate ZnCdS NCs-based WLED. The optical properties are investigated by ultraviolet-visible (UV-vis) absorption/fluorescence (FL) emission spectroscopy. Furthermore, the CIE chromaticity coordinates, CCT, CRI, and luminous efficiency of the prepared ZnCdS NCs-based WLEDs have been measured by integrating sphere system.

Figure S1 in supporting information (SI) shows the excitation and emission spectra of various ZnCdS NCs. It can be observed that the emission spectra of ZnCdS NCs are composed of two obvious peaks in which the sharper one is the band edge and the broader one is the surface state emission, resulting in the white light emission.[28,29] The ZnCdS NCs can be excited by a light source with the excitation wavelength less than 445 nm and the optimal excitation wavelength of various ZnCdS NCs is 370, 392, 398, 371, 381, 397, 358, 375 and 390 nm for DE-10, DE-30, DE-60, TDE-10, TDE-30, TDE-60, ODE-10, ODE-30 and ODE-60, respectively, implying that the WLEDs based on direct white light generation can be prepared by combining the UV chip (360-440 nm) with only one type of ZnCdS NCs layers. The emission wavelength on NCs can be easily tuned by reaction time and using different alkenes as surface ligands, which may affect the CIE and CCT of the ZnCdS NCs-based WLEDs.

The UV chip with an emission wavelength of 405 nm and open voltage at 2.8 V is used to excite the white light emitting ZnCdS NCs. Therefore, the WLEDs are prepared by the UV chip and ZnCdS NCs blended with UV resin under different weight ratios. Figure 1 shows the electroluminescence (EL) spectra of various ZnCdS NCs-based WLEDs with 10.0 and 50.0 wt. % of ZnCdS NCs content in the convert encapsulation types. It can be observed that the strong emission around 405 nm is from the UV chip and the relative intensity decreases as the NCs content increases. The emission spectra of DE-10, TDE-10, ODE-10 and ODE-30-based WLEDs are too narrow to emit white light because the emission wavelength of UV chip is not the appropriate excitation source of these four ZnCdS NCs as shown in Figure S1. Based on Figure S1 we can find that samples DE-60, TDE-60, and ODE-60 are suitable, while DE-10, TDE-10, and ODE-10 are not suitable to be excited by 405 nm, due to the low excitation intensity. In addition, as the NCs content increase, the emissions from ZnCdS NCs become stronger especially for surface state emission which may result in the decrease of CCT and the shift of chromaticity coordinates.

The optical properties of ZnCdS NCs-based WLEDs with different NCs contents including (x, y) chromaticity coordinates, CRI, CCT and luminous efficiency under a drive current of 20 mA are listed in Table S1 in SI and the chromaticity coordinates of ZnCdS NCs-based WLEDs with 10.0 and 50.0 wt. % of NCs content on the CIE 1931 chromaticity diagram are shown in Figure 2 (a) and (b), respectively. Although DE-10, TDE-10, and ODE-10 are not suitable to be excited by 405 nm due to the low excitation intensity as mentioned above, their high QY (DE-10 and TDE-10) and high content (50 %) can make the CRI, CCT, and efficiency of devices detectable. On the other hand, for DE-60, and TDE-60, and ODE-60, those samples are suitable to be excited by 405 nm, therefore the NCs with low QY can still have an efficiency between 2-4 lm/W. As a result, the high luminous efficiency > 4 lm/W can be observed by samples of DE-10, TDE-10, and ODE-10 with medium QYs and excitation conditions as show in Figure S1. It can be found out that the CCT decreases because not only the NCs content increases but also longer reaction time is applied. The shift of (x, y) chromaticity coordinates can be obtained by the different emission wavelengths of various ZnCdS NCs and the different NCs contents of ZnCdS NCs-based WLEDs as shown in Figure 2.The chromaticity coordinates of TDE-30 and ODE-30-based WLEDs with adding 50 wt. % of ZnCdS NCs are (0.34, 0.31) and (0.32, 0.30), respectively, close to the white light point (0.33, 0.33) as marked a star in Figure 2. Furthermore, the luminous efficiency of ZnCdS NCs-based WLEDs with 50 wt. % addition is slightly higher than those with 10 wt. % addition. The optimal conditions of the (x, y) chromaticity coordinates, CRI, CCT and luminous efficiency of WLEDs noted for ODE-30-based WLEDs is (0.32, 0.30), 82, 6811 K and 4.26 lm/W, respectively. The results show that the WLEDs based on direct white light generation can be prepared successfully by combining the UV chip with only one type of ZnCdS NCs layer and the CIE and CCT of ZnCdS NCs-based WLEDs can be tuned by different types of ZnCdS NCs from cold white to warm white. Chung et al. have pointed out that the luminous efficiency of single (580 nm) and dual (555+625 nm) quantum dots (QD) phosphors- based WLEDs excited by 460 nm blue chip is 5.62 and 3.79 lm/W at 20 mA, respectively. Their QYs are between 10~30 % with a CRI of 61.4.[30] Chandramohan et al. have found out that the luminous efficacy of the WLEDs composed with white CdSe NCs and blue chip is very low (less than 1 lm/W), compared to the devices made of core/shell type NCs (QY > 60 %), in part related to the fact of low QY (<5%).[31] In our study, the luminous efficiency of these ZnCdS NCs-based WLEDs seems to be related to the QY, emission and the optimal excitation wavelengths and concentrations of ZnCdS NCs.

Two encapsulation methods, convert and remote, with 50 wt. % NCs are used to investigate the optical properties of DE-30, DE-60, TDE-30, TDE-60, ODE-30 and ODE-60-based WLEDs and their EL spectra are shown in Figure 3. It can be observed that the emission peaks at 405 nm correspond to the EL of UV chip, the emissions between 410 and 445 nm are from the band edge emission of the NCs, and the broad emission across 450-700 nm comes from their surface state emission. The emission spectra of ZnCdS NCs-based WLEDs with remote type is different from those with convert type and the relative intensity of surface state emission decrease slightly while the band edge emission increase, maybe resulting from the non-uniformity of UV resin and NCs layers. Based on above results, it can be confirmed that the encapsulation method of the ZnCdS NCs strongly affects the properties of the devices.

The optical properties of ZnCdS NCs-based WLEDs with two encapsulation methods are listed in Table 1 and the chromaticity coordinates on the CIE 1931 chromaticity diagram are shown in Figure 4. The CCT of WLEDs with remote type is higher than those with convert type because of the less NCs content in the latter one. The luminous efficiency of ZnCdS NCs-based WLEDs can be slightly improved by the remote type maybe owing to the cover of UV resin on the UV chip so as to avoid the thermal quenching of NCs. As we have mentioned above that the melting point of capping reagents is lower than 60 ^{o}C, while the junction temperature of chip is higher than 100 ^{o}C. Therefore, luminous efficiency of remote-typed WLED is higher than that of convert-typed one. We have also found out that the similar tendency for remote-typed WLED, in which the appropriate excitation wavelengths of NCs with medium QYs have the highest luminous efficiency. Based on Figure 4, it can clearly find out that convert-typed WLED is close to warm light, while remote-typed one is in the cold light side and close to white light point, due to different NCs concentrations of in these two WLEDs is. It is also worth noting that the increase of CRI can be obtained by remote type, which reaches to 95 in TDE-60-based WLEDs. Besides, the properties of ZnCdS NCs-based WLEDs can be improved by the encapsulation methods. When the weight ratio of ZnCdS NCs is 50.0 wt. %, the optimal CIE, CRI, CCT, and luminous efficiency of ZnCdS NCs-based WLEDs prepared by convert and remote type are (0.32, 0.30), 82, 6811 K and 4.26 lm/W for ODE-30-based and (0.34, 0.33), 95, 5100 K and 3.50 lm/W for TDE-60-based WLEDs respectively. The CIE and CCT of the devices can be tuned by different types of ZnCdS NCs and NCs contents from cold white to warm white. Based on the above results, the WLEDs with high CRI can be obtained by remote encapsulation methods when ZnCdS NCs are used as nanophosphors.

Besides, the stability test of TDE-60 remote-type and ODE-30 convert-type devices are investigated. For the TDE-60 remote-type device, the stability is not good under 20 mA. The luminous efficiency decreases from 3.50 to 1.98 lm/W after 6 hr with a decay rate of 0.25 lm/W-hr and the photographs as shown in Figure S2 in SI. Figure S3 (left) in SI displays the EL spectra of this device during 6 hr stability test. It seems that after 6 hr, the CIE is out of white light range, CCT is increased, while CRI is decreased. We have found that the adhesion between UV gel and reflect cup is not good so that the film peels off easily. Besides, Figure S3 (right) in SI exhibits the EL spectra of TDE-60 remote-type device under different applied currents. When the applied current is increased from 5 to 50 mA, the luminous efficiency, CIE, CCT, and CRI changes from 2.77 to 1.30 lm/W, (0.35, 0.34) to (0.33, 0.29), 4420 to 5970 K, and 92 to 90, respectively. On the other hand, for the ODE-30 convert-type device, the luminous efficiency decreases from 4.26 to 3.54 lm/W after 20 hr as shown in Figure S4 (left) in SI. Its decay rate is 0.036 lm/W-hr under 20 mA, suggesting a better stability than TDE-60 remote-type device. CCT, CRI, and CIE are almost the same without any change. When the applied current is increased from 5 to 50 mA, the luminous efficiency, CIE, CCT, and CRI of ODE-30 convert-type device are changed from 4.55 to 2.42 lm/W, (0.40, 0.41) to (0.31, 0.29), 3760 to 7000 K, and 78 to 82, respectively as depicted in Figure S4 (right) in SI.

Conclusions

In this study, the ternary ZnCdS NCs with white light emission and high QYs have been prepared and used as nanophosphors in the fabrication of WLEDs in which the optical properties can be tuned by different contents of various ZnCdS NCs and the encapsulation methods. QYs, concentration of NCs, excitation wavelength, and encapsulation method affect the performance of ZnCdS NCs-based WLED. The optimal CIE, CRI, CCT, luminous efficiency, decay during stability test of ZnCdS NCs-based WLEDs prepared by convert and remote type are (0.32, 0.30), 82, 6811 K, 4.26 lm/W, 0.036 lm/W-hr, and (0.34, 0.33), 95, 5100 K, 3.50 lm/W, 0.25 lm/W-hr, respectively. As a result, the WLEDs assembled with only one type of ZnCdS NCs layers and UV chip have been demonstrated.

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Notes and references

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Table 1 The device properties of ZnCdS NCs-based WLEDs with two encapsulation methods.

Sample	type	CIE (x, y)	CRI	CCT (K)	Efficiency (lm/W)	QY (%)
DE-30	Convert	(0.39, 0.38)	81	3789	4.12	50.4
	Remote	(0.30, 0.28)	91	8157	4.82	
DE-60	Convert	(0.45, 0.43)	81	2997	2.92	25.3
	Remote	(0.33, 0.32)	93	6098	3.28	
TDE-30	Convert	(0.34, 0.31)	79	5178	4.34	48.7
	Remote	(0.32, 0.31)	85	6807	4.88	
TDE-60	Convert	(0.44, 0.42)	81	3085	3.30	34.6
	Remote	(0.34, 0.33)	95	5100	3.50	
ODE-30	Convert	(0.32, 0.30)	82	6811	4.26	38.7
	Remote	(0.28, 0.25)	81	14166	4.43	
ODE-60	Convert	(0.43, 0.43)	80	3355	3.67	36.2
	Remote	(0.30, 0.29)	93	7843	3.85	

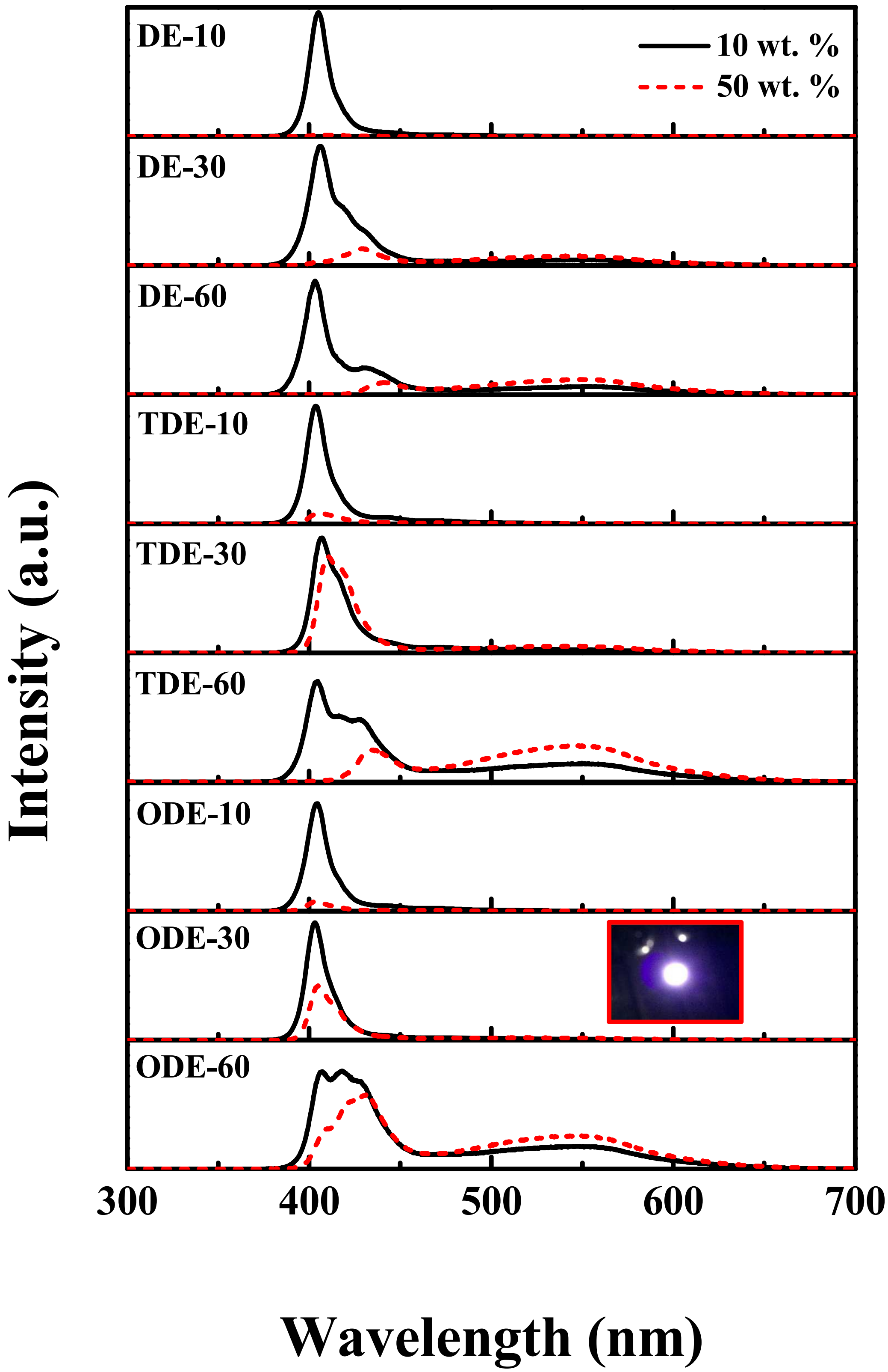

Figure 1 The EL spectra of various ZnCdS NCs-based WLEDs.

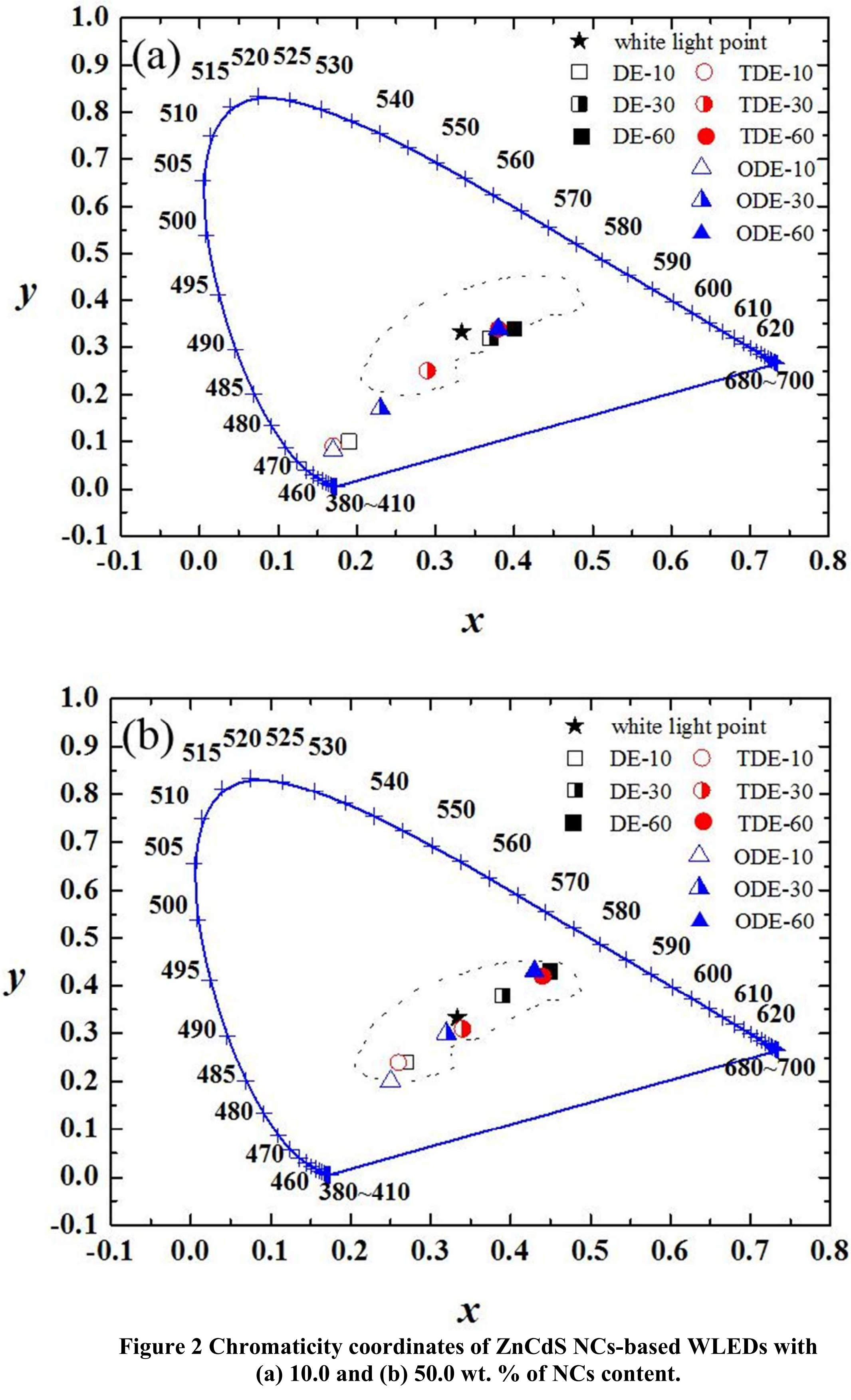

Figure 2 Chromaticity coordinates of ZnCdS NCs-based WLEDs with (a) 10.0 and (b) 50.0 wt. % of NCs content.

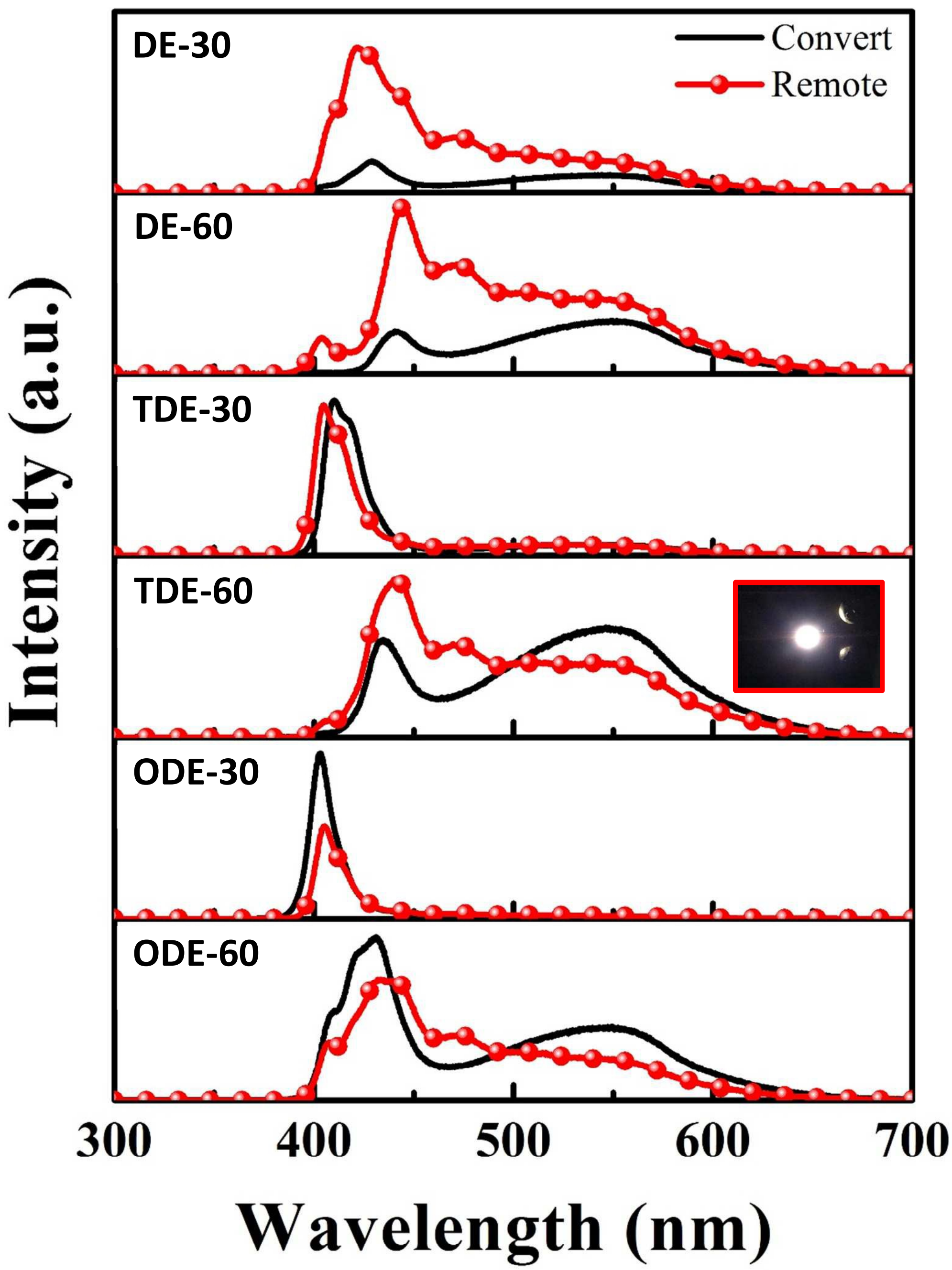

Figure 3 The EL spectra of various ZnCdS NCs-based WLEDs with two encapsulation methods.

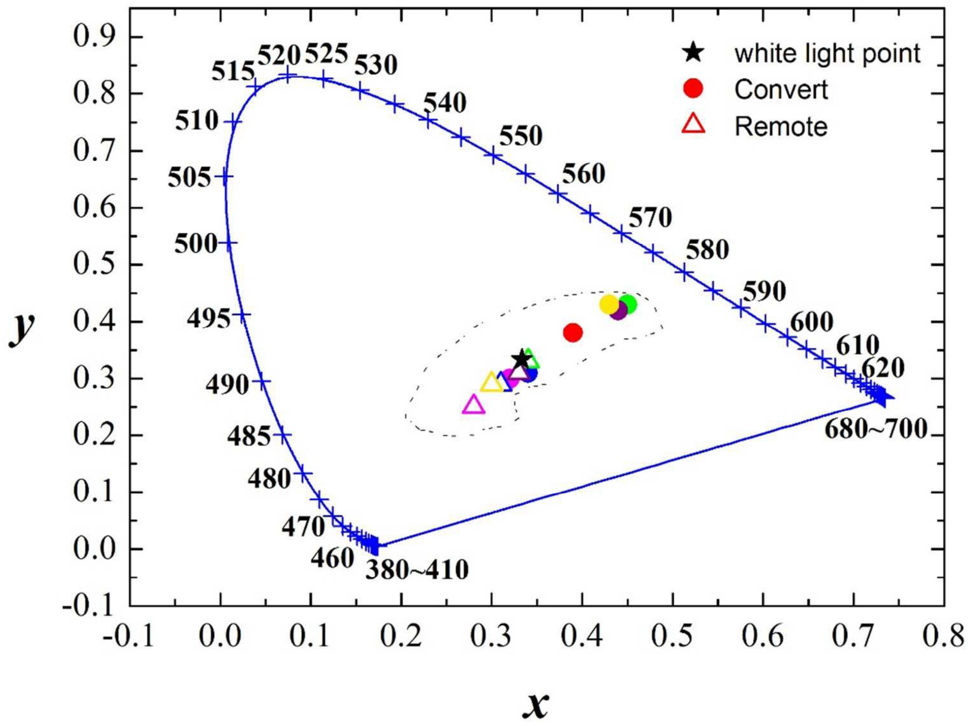

Figure 4 Chromaticity coordinates of ZnCdS NCs-based WLEDs with two encapsulation methods. ●: DE-30, ●: DE-60, ●: TDE-30, ●: TDE-60, ●: ODE-30 and ●: ODE-60.