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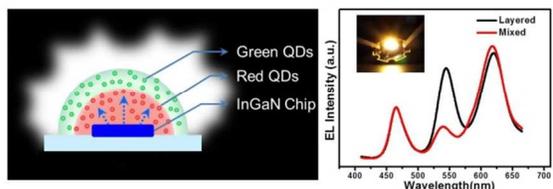
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Intrinsic quantum dots based white-light-emitting diodes with layered coating structure for reduced reabsorption of multiphase phosphors

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A white-light-emitting diode (WLED) with layered coating structure was successfully fabricated, providing a promising solution for the fabrication of intrinsic QDs based WLEDs with reduced reabsorption.

COMMUNICATION

Intrinsic quantum dots based white-light-emitting diodes with layered coating structure for reduced reabsorption of multiphase phosphors

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A white-light-emitting diode (WLED) with layered coating structure was fabricated by using intrinsic green-emitting and red-emitting CdSeS/CdS/ZnS core/multi-shell alloyed quantum dots as light conversion materials. The layered coating structure could efficiently reduce the reabsorption problem, and the as-prepared WLED exhibited good color rendering properties, providing a promising solution for the fabrication of intrinsic QDs based WLEDs with reduced reabsorption.

It has been reported that solid light emitting devices may reduce global electricity consumption by about 50%. InGaN-based light-emitting diodes (LEDs) solid-state lighting has been a rapidly growing area in illumination research and application, and the fabrication of white LEDs (WLEDs) have attracted more and more attention². Currently, rare-earth-based phosphors or organic phosphors are widely used as light conversion materials in commercial WLEDs. These phosphors, however, often suffer problems such as unstable against photo-oxidation or chemical environment, low color rendering index (CRI), scattering, *etc.*^{3,4} Quantum dots (QDs) are one of the most promising materials to improve the properties of WLEDs due to their size-tunable emission, broad absorption spectra, high photoluminescent quantum yield (PLQY), high stability and neglectable scattering effects.^{4,5,6,7} Many attempts have been made to fabricate WLEDs using II-VI group^{3,4,8}, III-V group^{6,9} or I-III-VI₂ group¹⁰ QDs as light conversion materials. Most of these WLEDs, however, were based on the intrinsic QDs which have small ensemble Stokes shift inducing a strong self-quenching effect and the reabsorption problem. This results in the intrinsic QDs based WLEDs with the same embarrassing problem as traditional phosphors and causes a decrease in the luminous efficiency of the WLEDs. As it has been reported¹¹, a WLED with a mixture QD-silica monoliths containing green-emitting and red-emitting CdSe/CdS/ZnS QDs together in the same silica matrix exhibited a 30% less efficacy than that with the separately prepared green and red QDs-silica monoliths due to reabsorption between the densely located green and red QDs in the network. Although Wang *et al.*¹² successfully fabricated a WLED by using a combination of Cu:CdS/ZnS doped QDs and YAG:Ce

phosphor to avoid the reabsorption and improve the CRI, this WLED contained conventional phosphors which might still suffer the problem of scattering. In comparison with intrinsic QDs, the limited types of doped QDs with high PLQY and tunable wavelength also limit their application in WLEDs. Therefore, it is challenging to fabricate a intrinsic QDs based WLED with reduced reabsorption in the absence of the conventional phosphors.

Figure 1(a) shows a typical structure of QD-LED, in which a blue InGaN LED chip is covered by hemispherical QDs/epoxy composite, and the QDs with different emission wavelengths are dispersed in epoxy resin. In this structure, the red-emitting QDs would absorb both the green light from green-emitting QDs and blue light from LED chip (see **Figure 2(a)**), which will inevitably result in serious reabsorption problem. Recently, Shinae Jun *et al.*¹³ reported that the separation of the light conversion materials with different wavelengths could efficiently reduce the reabsorption problem. To combine the advantages of QDs and the separated layer coating structure, we tried to fabricate a WLED with structure as **Figure 1(b)**. In this structure, a green-emitting QDs/epoxy outer layer and a red-emitting QDs/epoxy inner layer are combined with a blue InGaN LED chip. The 460nm emission from the LED chip would be partially absorbed by the red-emitting QDs and forming a mixed light with blue and red light in the inner layer. When the mixed light goes through the outer layer, another part of the blue light would be absorbed and the green light would be excited subsequently, resulting in a white light composed of blue, green and red light with reduced loss of green light. Though path of the green light is in all direction and the inner-ward part would still be partially reabsorbed by the red-emitting QDs, this structure might efficiently reduce the reabsorption problem because the red-emitting QDs have no influence on the outward part of the green light.

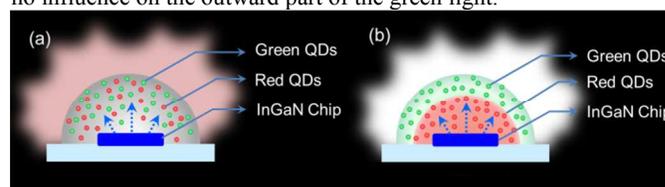


FIG. 1. Schematic diagram of QDs based WLED fabricated by (a) mixing method and (b) layered coating method.

As a proof of concept, ternary alloyed CdSeS QDs were used as light conversion materials in our study. Ternary QDs have attracted more and more interest in recent years for their optical and electronic properties can be tuned not only by the particle size, but also by the composition of the alloyed QDs. Among all the II-VI ternary QDs, CdSeS QD is one of the most promising QDs as light conversion material for WLEDs due to its broad tunable wavelength covering the visible light range. Herein, we synthesized the CdSeS/CdS/ZnS core/multi-shell QDs with different Se/S ratio via a phosphine-free route in paraffin liquid. (see Experimental section). The absence of phosphine or alkyl-phosphine such as TOP, TOPO and TBP during the synthesis makes the process cheaper and environmental-friendly, and the core-shell-type QDs were synthesized due to their enhanced PLQYs and greater tolerance to the processing conditions necessary for device fabrication. The wavelength of the as-prepared CdSeS/CdS/ZnS core/multi-shell QDs could be tuned in the wide range of 440 ~ 625nm by simply changing their size and composition (see **Figure S1**), and the as-prepared green-emitting CdSe_{0.4}S_{0.6}/CdS/ZnS QDs (PL peak of 540 nm, PLQY of 55%) and red-emitting CdSe_{0.9}S_{0.1}/CdS/ZnS QDs (PL peak of 612 nm, PLQY of 45%) were used as light conversion materials to fabricate the WLEDs. The PL and absorption spectra of the green-emitting and red-emitting QDs are shown in **Figure 2(a)**. It could be seen that both of their full width at half maximums (FWHMs) are about 30nm, indicating their narrow size distribution. The transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images (see **Figure 2 c,d**) also show the homogeneity of the as-prepared QDs, and the sizes of green-emitting and red-emitting QDs are about 5.4 nm and 5.6 nm, respectively, indicating their different wavelengths resulted from the changing of the composition instead of the size. The well-resolved lattice fringes (the inset in **Figure 2 c,d**) confirm the good crystallinity of the as-prepared QDs. The lattice parameters of (1 1 1), (2 2 0) and (3 1 1) from the selected area electron diffraction(SAED) illustrate that the as-prepared QDs have cubic zinc blended structure, which could be also confirmed by the results of X-ray diffraction (XRD) analysis (**Figure 2b**). Their distinct diffraction peaks locate between the peaks of CdSe and CdS, which would shift with the Se/S ratio in the QDs, indicating the alloy of CdSeS. The peaks of the red-emitting QDs with more Se molar fraction would shift to larger Bragg angles, which is closer to that of CdSe and agrees well with the results of the literatures.¹⁴

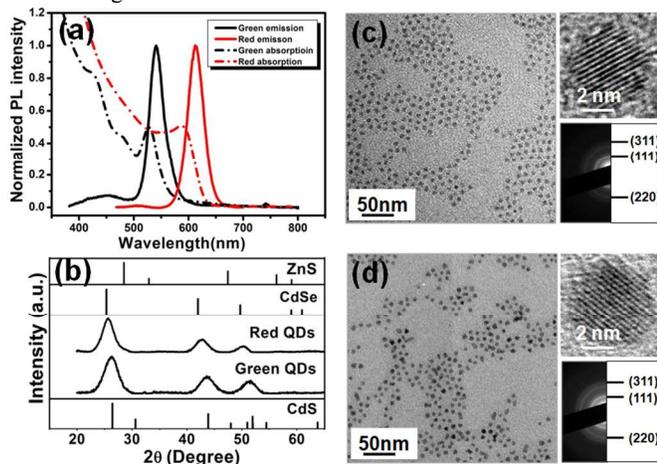


FIG. 2. (a) PL and UV-vis absorption spectra of green and red-emitting QDs; (b) XRD patterns of green and red-emitting QDs; TEM, HRTEM and SAED images of the green-emitting QDs (c) and the red-emitting QDs (d).

Then the green emitting QDs/epoxy and the red emitting QDs/epoxy were solidified separately onto the 460nm InGaN chip to fabricate the WLED with layered coating structure (see Experimental section). As for indoor residential illumination, a color temperature of 2700 k to 3300 k is normally preferred, and the ratio of the blue, green and red light was adjusted to form a white light that is similar to 2700K blackbody in our study. As shown in the inset of **Figure 3(a)**, white light could be emitted from the layered-coating structure WLED with a CRI of 91.3 under 140mA forward bias current, which is much higher than Ce³⁺: YAG based commercial white LED (Ra-70), and the color temperature of the WLED is 2576K corresponding to a warm white light. The electroluminescence (EL) spectra of the WLED operated at forward bias currents from 20 to 200 mA present a 460nm emission band from the blue InGaN LED chip and two emission bands located at 540nm and 625nm corresponding to the emissions of the green and red QDs, respectively. The EL spectra of the LED fabricated by directly mixing the green and red QDs together with the same QDs ratio and amount are shown in **Figure 3(b)** for comparison, which exhibit a much redder light (inset of **Figure 3(b)**) at 140mA than the layered coating structure one due to the reabsorption of the green light. It could be seen from **Figure S2** that the green emission of the WLED fabricated by directly mixing the QDs under 140mA forward bias current suffers about 63% loss in intensity compared to that of the layered coating structure WLED, indicating the layered coating structure could efficiently reduce reabsorption of multiphase phosphors.

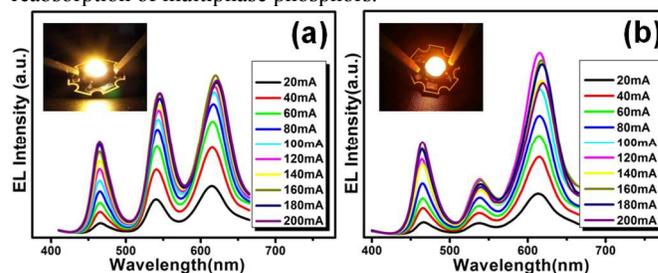


FIG. 3. EL spectra of the CdSeS/CdS/ZnS QDs based WLED fabricated by (a) layered coating method and (b) mixing method operated under different forward bias currents.

Moreover, the power efficiency (PE) of the as-prepared layered coating structure WLED presented a much higher value of 32.5 $\text{lm} \cdot \text{W}^{-1}$ at 140 mA than the incandescent light bulbs ($\text{PE} < 18 \text{ lm} \cdot \text{W}^{-1}$). It could also be seen that the CIE (International Commission on Illumination) color coordinates and the CRI of the layered coating structure WLED presented a little change under different forward bias currents, indicating good optical stability of the output light of the WLED. In comparison with the WLED fabricated by directly mixing the QDs together with the same QDs ratio and amount, it could be obviously seen that there are distinct loss in PE and CRI when green light is reabsorbed by the red-emitting QDs. The enhancement of the PE and CRI under 140mA forward bias current are 47% and 18.6%, respectively, indicating that the layered coating structure is efficient to improve the properties of the WLEDs. Furthermore, as shown in **Figure 4(d)**, the higher CRI of the layered coating structure WLED mainly results from the improvement of R2-R3. The temperature-related luminescence properties of the CdSeS/CdS/ZnS QDs based WLED fabricated by layered coating method was also investigated at the temperature ranged from 10°C to 160°C. As shown in **Figure S3(a)**, the QDs/epoxy composites demonstrate good thermal stability and can still remain over 80% of initial PL intensity even at the temperature higher than 150°C. The properties of layered coating structure WLED (see **Figure S3(b-d)**) also show good stability under different temperature, indicating its

promising application. Moreover, different from the broad EL spectra of YAG:Ce-QDs based WLEDs^{7, 12, 15}, our layered coating structure WLED shows sharp EL spectra with full widths at half maximum (FWHMs) of less than 40 nm, which demonstrates obvious advantage in the application of LCD TV backlight sources.

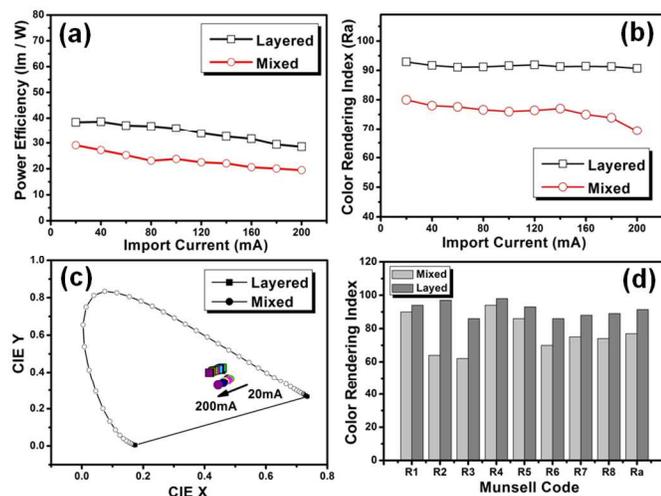


FIG. 4. PE (a), CRI (b), and the CIE color coordinates (c) of the as-prepared QDs-WLED fabricated by layered coating method and mixing method under different forward bias currents; (d) Munsell code corresponding to different CRI of WLEDs fabricated by mixing method and layered coating method at 140 mA.

Conclusions

In summary, CdSeS/CdS/ZnS core/multi-shell QDs were successfully synthesized via a phosphine-free route. A WLED with layered coating structure was fabricated based on green and red emitting CdSeS/CdS/ZnS core/multi-shell QDs and a blue InGaN LED chip, which greatly decreased the reabsorption of multiphase phosphors. The as-fabricated WLED can improve the PE and color rendering by about 47% and 18.6% compared to the mixing method fabricated WLEDs at 140 mA. Moreover, the WLED with the layered coating structure also showed good color chromatics stability, indicating the layered coating structure a promising solution for the fabrication of intrinsic QDs based WLEDs with good color rendering properties.

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Notes and references

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Electronic Supplementary Information (ESI) available: [experimental details, PL spectra and photographs of the CdSeS/CdS/ZnS core/multi shell QDs, and comparison of EL spectra of the as-prepared QDs-WLED fabricated by layered coating method and mixing method at 140mA]. See DOI: 10.1039/c000000x/

1. C. J. Humphreys, *MRS bulletin*, 2008, **33**, 459-470.
2. M. R. Krames, O. B. Shchekin, R. Mueller-Mach, G. O. Mueller, Z. Ling, G. Harbers and M. G. Craford, *Display Technology, Journal of*, 2007, **3**, 160-175; J. W. Orton and C. T. Foxon, *Reports on Progress in Physics*, 1998, **61**, 1-75; J. K. Park, C. H. Kim, S. H. Park, H. D. Park and S. Y. Choi, *Appl. Phys. Lett.*, 2004, **84**, 1647; F. Hide, P. Kozodoy, S. P. DenBaars and A. J. Heeger, *Appl. Phys. Lett.*, 1997, **70**, 2664; R.-J. Xie, N. Hirotsaki, M. Mitomo, K. Takahashi and K. Sakuma, *Appl. Phys. Lett.*, 2006, **88**, 101104.
3. X. Wang, W. Li and K. Sun, *J. Mater. Chem.*, 2011, **21**, 8558.
4. H. S. Jang, H. Yang, S. W. Kim, J. Y. Han, S.-G. Lee and D. Y. Jeon, *Adv. Mater.*, 2008, **20**, 2696-2702.
5. S. Nizamoglu, E. Mutlugun, T. Özel, H. V. Demir, S. Sapra, N. Gaponik and A. Eychmüller, *Appl. Phys. Lett.*, 2008, **92**, 113110; E. Jang, S. Jun, H. Jang, J. Lim, B. Kim and Y. Kim, *Adv. Mater.*, 2010, **22**, 3076-3080; I.-K. Park, M.-K. Kwon, J.-O. Kim, S.-B. Seo, J.-Y. Kim, J.-H. Lim, S.-J. Park and Y.-S. Kim, *Appl. Phys. Lett.*, 2007, **91**, 133105.
6. X. Yang, Y. Divayana, D. Zhao, K. Swee Leck, F. Lu, S. Tiam Tan, A. Putu Abiyasa, Y. Zhao, H. Volkan Demir and X. Wei Sun, *Appl. Phys. Lett.*, 2012, **101**, 233110.
7. J.-U. Kim, Y.-S. Kim and H. Yang, *Mater. Lett.*, 2009, **63**, 614-616.
8. B.-H. K. Ho Seong Jang, Heesun Yang, Duk Young Jeon, *Appl. Phys. Lett.*, 2009, **95**, 161901; S. Sapra, S. Mayilo, T. A. Klar, A. L. Rogach and J. Feldmann, *Adv. Mater.*, 2007, **19**, 569-572; S. Nizamoglu, T. Ozel, E. Sari and H. Demir, *Nanotechnology*, 2007, **18**, 065709; M. A. Schreuder, K. Xiao, I. N. Ivanov, S. M. Weiss and S. J. Rosenthal, *Nano Lett.*, 2010, **10**, 573-576; S. Nizamoglu, E. Mutlugun, O. Akyuz, N. K. Perkgoz, H. V. Demir, L. Liebscher, S. Sapra, N. Gaponik and A. Eychmüller, *New Journal of Physics*, 2008, **10**, 023026; L. Zhu, L. Xu, J. Wang, S. Yang, C.-F. Wang, L. Chen and S. Chen, *RSC Advances*, 2012, **2**, 9005-9010.
9. K. Kim, S. Jeong, J. Y. Woo and C.-S. Han, *Nanotechnology*, 2012, **23**, 065602; S. Kim, T. Kim, M. Kang, S. K. Kwak, T. W. Yoo, L. S. Park, I. Yang, S. Hwang, J. E. Lee and S. K. Kim, *J. Am. Chem. Soc.*, 2012, **134**, 3804-3809; J. Ziegler, S. Xu, E. Kucur, F. Meister, M. Batentschuk, F. Gindele and T. Nann, *Adv. Mater.*, 2008, **20**, 4068-4073; E.-P. Jang and H. Yang, *J. Nanosci. Nanotechnol.*, 2013, **13**, 6011-6015.
10. J.-H. Kim and H. Yang, *Nanotechnology*, 2014, **25**, 225601; W.-S. Song, S.-H. Lee and H. Yang, *Optical Materials Express*, 2013, **3**, 1468-1473; W.-S. Song and H. Yang, *J. Nanosci. Nanotechnol.*, 2013, **13**, 6459-6462; J.-H. Kim, W.-S. Song and H. Yang, *Opt. Lett.*, 2013, **38**, 2885-2888; H. Kim, J. Y. Han, D. S. Kang, S. W. Kim, D. S. Jang, M. Suh, A. Kirakosyan and D. Y. Jeon, *J. Cryst. Growth*, 2011, **326**, 90-93; W. Chung, H. Jung, C. H. Lee and S. H. Kim, *J. Mater. Chem. C*, 2014, **2**, 4227-4232; W.-S. Song and H. Yang, *Chem. Mater.*, 2012, **24**, 1961-1967.
11. S. Jun, J. Lee and E. Jang, *ACS Nano*, 2013, **7**, 1472-1477.
12. X. Wang, X. Yan, W. Li and K. Sun, *Adv. Mater.*, 2012, **24**, 2742-2747.
13. H. S. J. Yu-Ho Won, Kyoung Woo Cho, Yong Seon Song, Duk Young Jeon, Ho Ki Kwon, *Opt. Lett.*, 2009, **34**, 1-3.
14. H.-J. Zhan, P.-J. Zhou, R. Ma, X.-J. Liu, Y.-N. He and C.-Y. Zhou, *J. Fluoresc.*, 2013, 1-9; H. Qian, L. Li and J. Ren, *Mater. Res. Bull.*, 2005, **40**, 1726-1736; J. Ouyang, M. Vincent, D. Kingston, P. Descours, T. Boivineau, M. B. Zaman, X. Wu and K. Yu, *The Journal of Physical Chemistry C*, 2009, **113**, 5193-5200.
15. X. Xu, Y. Wang, W. Xia, L. Zhou, F. Gong and L. Wu, *Mater. Chem. Phys.*, 2013, **139**, 210-214.