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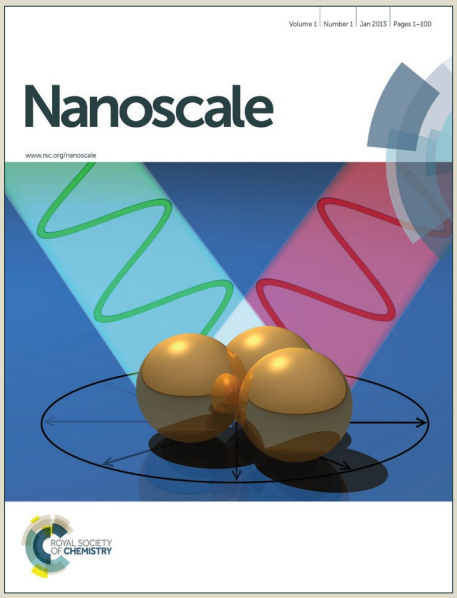

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COMMUNICATION

Doped quantum dot@silica nanocomposites for white light-emitting diodes

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This work reports the use of a near-UV-LED chip in combination with blue, greenyellow and red emitting doped ZnSe QD@silica nanocomposites to construct a novel WLED with reduced scattering and no reabsorption. Blue, green-yellow and red emitting Cu or Mn doped ZnSe QDs with enlarged Stokes shifts and similar absorption peaks (360-410 nm) were synthesized in liquid paraffin in order to solve the reabsorption problem and also obtain balanced white emission spectra. Silica shells were then coated onto the doped QDs, allowing for the refractive index of the nanocomposites to be tailored while simultaneously improving their compatibility with the epoxy resin. The transparent doped ZnSe QD@SiO_2 /epoxy composite was then used as a light conversion and encapsulant material in combination with near-UV-LED chip to fabricate the WLED. This fabricated WLED demonstrated high luminous efficiency and good color chromatics stability, suggesting that WLEDs based on highly fluorescent doped ZnSe QD@silica nanocomposites in combination with near-UV-LED chips may prove to be promising candidates for alternative light sources.

Introduction

Solid-state white light-emitting diodes (WLEDs) are attractive replacements for current illumination devices due to their longer service lifetime, lower thermal resistance, more compact size and higher efficiency.[1] The commercial white light source, however, is usually based on YAG:Ce phosphor with a blue emitting InGaN LED chip and has a low color rendering index (CRI~70) with color deficiencies in the red and green regions.[2] One of the most promising solutions for this problem is to use a near-UV-LED chip (360-410 nm) in combination with blue, green and red light-emitting phosphors to provide a more balanced white emission spectrum and a higher color rendering index.[2] However, the reabsorption of multi-phased phosphors can lead to a decrease of luminous efficiency.[3, 4] WLEDs containing a near-UV LED chip and a single phase full-color emitting phosphor are also a potential solution. Previous work demonstrates that phosphors possessing high efficiencies during near UV excitation are still rare resulting in lower luminous efficiencies for WLEDs.[5, 6]

Quantum dots (QDs) with unique properties such as size-tunable emissions, broad absorption spectra, high photoluminescent quantum yields (PL QYs), high stabilities and negligible scattering effects[7-11] , have attracted great attention and been used as light conversion materials to replace traditional phosphors.[4, 7, 12-33] However, most of these WLEDs have been based on intrinsic QDs with small ensemble Stokes shifts, which induce a strong self-quenching effect and the reabsorption problem, resulting in WLEDs with the same problems as traditional phosphors as well as decreased luminous efficiency.[4]

Recently, doped intrinsic QDs containing transition metal ions have been widely explored because of their unique optical properties.[34-38] Doped QDs not only retain nearly all the advantages associated with intrinsic QDs but also possess new properties such as enhanced thermal stability and reduced chemical sensitivity. Doped QDs also have enlarged Stokes shifts due to absorption/energy transfer, eliminating the previously mentioned self-quenching and reabsorption problems.[34, 35] The unique properties of doped QDs provided us with the idea to construct a novel WLED by using a near-UV-LED chip in combination with blue, green and red emitting doped QDs, which may not suffer reabsorption resulting from interactions between the individual components. Our previous work[39] reports that WLEDs without any reabsorption problems can be successfully fabricated by using Cu:CdS doped QDs and YAG:Ce phosphors. However, these WLEDS were found to have a limited emission range from red to deep red. Additionally, Peng et al.[34, 35] found that the PL wavelength of Cu and Mn doped ZnSe QDs span a range of 470 nm to 610 nm, with an absorption peak around 400 nm due to the bandgap of the ZnSe QDs. Moreover, the absence of heavy metal elements makes these QDs more environmentally friendly. Therefore, the enlarged Stokes shift with suitable near-UV absorption coupled with the absence of heavy metal elements potentially makes Cu and Mn doped ZnSe QDs better light conversion materials for WLEDs based on near-UV-LED chips. Recently, Eychmüller et al. reported the synthesis of white-light emitting doubly doped Cu, Mn:ZnSe QDs through a hot-injection colloidal approach.[40] However, these doubly doped QDs

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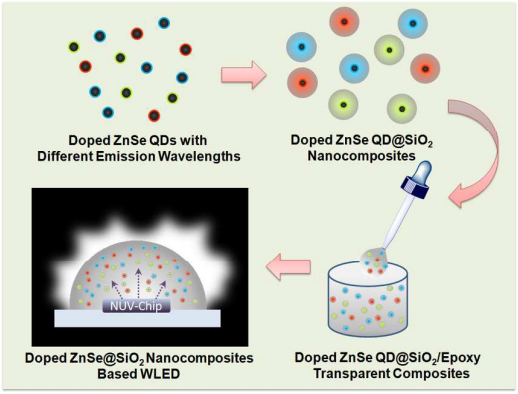
lack the green component of the visible spectrum and possess relatively low PL QYs,[40] which may limit their further application.

Phosphor scattering is another common problem that often limits the application of LEDs. Though nano-scale QDs may not suffer from scattering problems theoretically, the relatively high concentration and the incompatibility of the QDs with the epoxy polymer may lead to the aggregation of the QDs [41] and cause scattering as a result. Moreover, the mismatch between the refractive indices (RIs) of the QDs and the epoxy polymer can also cause scattering problems. Additional surface treatment of QDs, in particular coating of QDs with a silica shell, can help prevent aggregation.[41] Furthermore, Gu et al.[42] reported that the RI of nanoparticles with a core/shell structure can be tuned by changing the ratio of the individual components. Fu et al.[43] successfully adjusted the refractive index of TiO_2@SiO_2 nanoparticles to fabricate transparent TiO_2@SiO_2/polymer composites. Since the refraction index of epoxy resin (~1.52[44]) is between that of silica(~1.42[45]) and ZnSe(~2.89[46]), it can be expected that a transparent doped ZnSe QDs@SiO_2/epoxy composite could be developed by adjusting the ratios of the components, allowing the composite to act as both a light conversion and encapsulant material while simultaneously preventing aggregation of the QDs.

In this work, we report the use of a near-UV-LED chip in combination with blue, green-yellow and red emitting doped ZnSe QD@silica nanocomposites in order to construct a novel WLED (see Scheme 1) with reduced scattering and no reabsorption. Blue, green-yellow and red emitting Mn or Cu doped ZnSe QDs with enlarged Stokes shifts and similar absorption peaks (360-410 nm) were synthesized to solve the reabsorption problem and obtain balanced white emission spectra. Silica shells were then coated onto the d-dots, allowing for the refractive index of the nanocomposites to be adjusted while simultaneously improving their compatibility with the epoxy resin. The doped QD@SiO_2/epoxy composite



Scheme 1. Schematic diagram for the preparation of WLEDs based on doped ZnSe QD@SiO_2 nanocomposites.

was then fabricated as a light conversion and encapsulant material in combination with near-UV-LED chip in order to fabricate the WLED. This WLED demonstrated high luminous efficiency and good color chromatics stability, suggesting that WLEDs based on highly fluorescent doped QD@silica nanocomposites and near-UV-LED chips may prove to be promising candidates for alternative light sources.

Results and discussion

To apply doped ZnSe QDs in WLEDs, growth-doping and nucleation-doping strategies were used to fabricate Cu:ZnSe and Mn:ZnSe doped QDs, respectively, with various emission colors in a cheap long chain alkane solvent of liquid paraffin successfully (see Experimental section for details). As is well known, energy transfer plays an important role in the optical properties of luminescent materials, and their illumination performance is bound up with the local structures around activated ion centres[47-51]. Different emission wavelengths for the Cu:ZnSe doped QDs can be obtained by tailoring their particle size during their synthesis. It is generally agreed that the emission from the Cu dopant in ZnSe results from the radiative recombination between electrons located at the bottom of the host conduction band as well as the holes localized in the Cu T_2 states.[52] Therefore, emission peaks can be tuned by changing the bandgap of the host, which is determined by particle size. In our experiments, the particle size of the Cu:ZnSe QDs is tailored by altering the reaction time in order to obtain Cu:ZnSe QDs with blue to greenish yellow emission colors (see Fig. 1a). In contrast with Cu doping, doping Mn into a ZnSe host leads to mixing with the wide $^4T_1$ to $^6A_1$ energy gap of Mn.[53] Thus the emission peak wavelength of the Mn:ZnSe QDs can only be tuned within a very limited range around 580 nm, which is insufficient for application as the red component in WLEDs. To obtain Mn:ZnSe QDs with a larger range of emission peak wavelengths, the lattice field around a given Mn center within the QDs must be more symmetric, resulting in a smaller energy level splitting[34, 35].Therefore, based on previous literature,[35] thiol ligands of 1-dodecanethiol (DDT) were added to the reaction

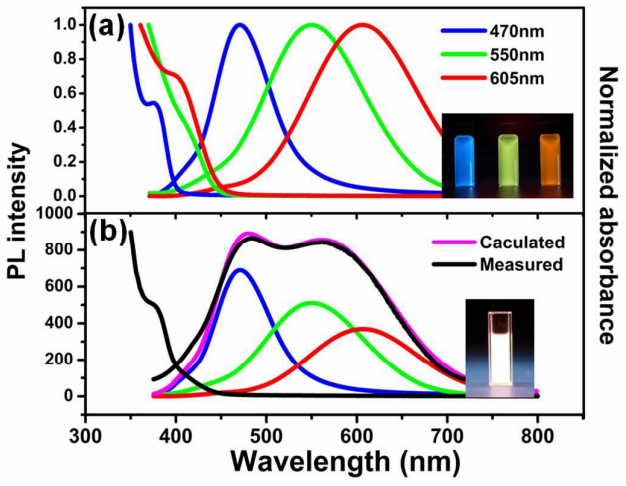


Fig. 1 (a) PL and UV-vis absorption spectra of doped ZnSe QD solutions with emission peaks at 470 nm (Cu: ZnSe QDs), 550 nm (Cu: ZnSe QDs) and 605 nm (Mn: ZnSe QDs). Insert shows doped ZnSe QD solutions under 365 nm UV light; (b) PL spectra of doped ZnSe QD solutions before mixing and PL and UV-vis absorption spectra of doped ZnSe QDs after mixing. Insert shows the doped ZnSe QDs under 365 nm UV light.

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mixture to tune the color of the Mn:ZnSe QDs. As a result, the PL peak wavelength of the Mn:ZnSe QDs showed a significant red-shift from 580 nm to 605 nm without any change of their absorption spectra after the ligand exchange (see Fig. S1). PL and UV-vis absorption spectra of the Cu:ZnSe (~470nm, 550nm) and Mn:ZnSe (~605nm) doped QDs from our experiments are shown in Fig. 1a. These spectra show that there is no intrinsic bandgap emission observed for the ZnSe QDs, indicating the successful doping of Cu or Mn into the ZnSe QDs. The PLQYs of the prepared doped ZnSe QDs with emission peaks at 470 nm, 550 nm and 605 nm are 30%, 51% and 57%, respectively. All of the doped ZnSe QDs showed similar absorption peaks around 400 nm and bright fluorescence was observed from their solutions when exposed to 365 nm UV light (see insert of Fig. 1a). These results indicate that the doped ZnSe QDs can act as blue, green-yellow and red components of WLEDs with near-UV chips.

We also specifically investigated the reabsorption problem of the Cu:ZnSe and Mn:ZnSe doped QDs with emission wavelengths of 470 nm, 550 nm and 605 nm, which were mixed with a molar ratio of 5:2:1 to obtain a wave pattern similar to natural sunlight (see Fig. 1b).[54] The measured spectrum fit well with the calculated one without any observed reabsorption, demonstrating the potential benefit of using the Cu and Mn doped ZnSe QDs as light conversion materials. Due to the large Stokes shifts of the Cu and Mn doped ZnSe QDs and their similar absorption peaks around 400 nm, there does not appear to significant overlaps between the PL and UV-vis spectra of the Cu and Mn doped ZnSe with different emission wavelengths. These results indicate that light with shorter emission wavelengths is not absorbed by the QDs with longer emission wavelengths, facilitating the facile design of the desired white light spectrum. Bright white light is observed under 365 nm UV irradiation (see insert of Fig. 1b) with a wave pattern similar to natural sunlight and a high CRI value of 96. Due to their appropriately sized bandgaps and enlarged Stokes shift, the application of these doped ZnSe QDs in near-UV chip based WLEDs allows for high color rendering properties to be obtained without inducing any reabsorption.

Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images (see Fig. 2a) show the homogeneity of the prepared doped ZnSe QDs. From these images, the average sizes of the Cu:ZnSe and Mn:ZnSe QDs with wavelengths of 470 nm, 550 nm, 605 nm were determined to be approximately 3.8 nm, 5.2 nm and 5.0 nm, respectively (see Fig. S2 for their size distributions). The well-resolved lattice fringes in these images confirm the good crystallinity of the prepared QDs. Lattice parameters of (1 1 1), (2 2 0) and (3 1 1) from the selected area electron diffraction (SAED) illustrate that the doped ZnSe QDs have a cubic zinc blended structure. These results were also confirmed by X-ray diffraction (XRD) (Fig. 2b). There are almost no differences observed in the XRD results for the doped ZnSe QDs and the intrinsic ZnSe QDs, indicating that Cu and Mn doping have little influence on the matrix crystal structure.

We also synthesized doped ZnSe QD@SiO_2 nanocomposites in order to address the scattering problem of QDs in WLEDs. This scattering usually results from either the aggregation of QDs due to

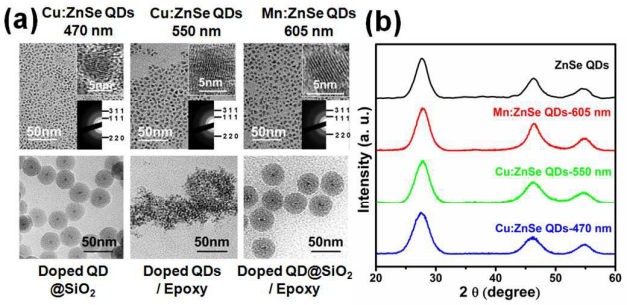

Fig. 2 (a) TEM, HRTEM, and SAED images of doped ZnSe QD solutions with emission peaks at 470 nm (Cu: ZnSe QDs), 550 nm (Cu: ZnSe QDs) and 605 nm (Mn: ZnSe QDs) (top) and TEM images of Mn: ZnSe QD@SiO_2 nanocomposites, Mn: ZnSe QDs in epoxy and Mn: ZnSe QD@SiO_2 nanocomposites in epoxy (bottom); (b) XRD patterns of intrinsic ZnSe QDs and doped ZnSe QDs with emission peaks at 470 nm (Cu: ZnSe QDs), 550 nm (Cu: ZnSe QDs) and 605 nm (Mn: ZnSe QDs).

the presence of hydrophobic ligands on the QD surfaces that are incompatible with the epoxy resin or significant differences between the refractive indices (RI) of the QDs and the epoxy resin. According to previous literature,[43, 55] the reduction in the transmitted light intensity from the particles embedded within the polymer can be described as follows:

$$\frac{I}{I_0} \propto \exp\left[\frac{-3V_p x r^3}{4\lambda^4}\left(\frac{n_p}{n_r}-1\right)\right] \quad (1)$$

where I and I_0 are the light intensity of the polymer with and without the embedded particles, respectively. V_p is the volume fraction of the particle, whereas x is the optical path length, r is the radius of the particle, λ is the wavelength of the light, and n_p and n_r are the RIs of the particle and the polymer, respectively. According to Eq.1, the RI of the embedded particles must be similar to that of the polymer in order to avoid any reduction in light intensity and result in a transparent composite. According to previous calculations of the RI of composites,[42, 43, 56] the RI of the QDs@SiO_2 nanocomposites can be tailored by changing the volume fraction of the silica and QDs, calculated as:

$$n^2_{composite} = \sum_i n_i^2 V_i \quad (2)$$

where $n_{composite}$ is the RI of the nanocomposites and V_i and n_i are the volume fraction and RI of the individual components, respectively. In our previous work,[57] we reported the synthesis of CdSe/CdS/ZnS@SiO_2 nanoparticles with particle sizes ranging from 30 to 50 nm by a reverse emulsion method. In this work, Cu:ZnSe and Mn:ZnSe doped QDs were used instead of CdSe/CdS/ZnS intrinsic QDs to successfully make QD@SiO_2 nanocomposites (see Experimental section for details). The resultant doped ZnSe QD@SiO_2 nanocomposites retain over 70% of their initial PL intensities with little change in their PL peak positions (see Fig. S3). The TEM image of the Mn:ZnSe QD@SiO_2 nanocomposites is shown in Fig. 2a (bottom left). We observed that the average diameter of the nanocomposites is 32±2 nm. With the previously reported RI

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values of the epoxy resin (1.52 [49, 50]) [43, 44], ZnSe QDs (2.89 [46]) and silica (1.42[58, 59]), we can use Eq. 2 to calculate a RI value for the

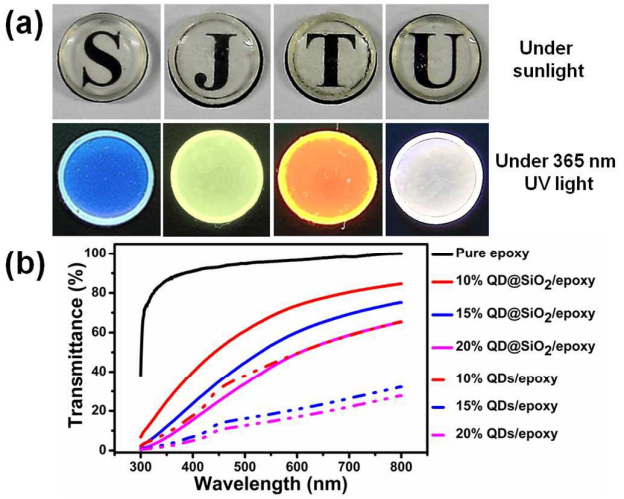

Fig. 3 (a) Images of the blue, green-yellow, red and white light emitting doped ZnSe QD@SiO_2 /epoxy composite films under sunlight (top) and 365 nm UV light (bottom); (b) UV-vis transmittance spectra of the epoxy matrix, Mn:ZnSe QD/ epoxy and Mn:ZnSe QD@SiO_2/epoxy composite films (the diameter and the thickness of the samples are 10 mm and 1 mm, respectively).

doped ZnSe QD@SiO_2 nanocomposites of 1.43. Compared to the ZnSe QDs without a silica shell, the difference in the RIs of the nanocomposites and the epoxy resin is effectively reduced by 93%.

These doped ZnSe QD@SiO_2 nanocomposites were then mixed with the epoxy resin in order to synthesize the nanocomposite/epoxy composites (see Experimental section for details). Images of the doped ZnSe QD@SiO_2/epoxy composites illuminated by sunlight and 365 nm UV irradiation are shown in Fig. 3a. Due to the similar RIs of the doped ZnSe QD@SiO_2 nanocomposites and the epoxy, the composites appear highly transparent and colorless in sunlight. However, due to their near-UV absorption and high PL yields, strong emission by the doped ZnSe QD@SiO_2/epoxy composites is observed under 365 nm UV irradiation. Transmission spectra of the doped ZnSe QD@SiO_2/epoxy composites were measured and compared to the corresponding doped ZnSe QDs/epoxy composites (see Fig. 3b). The transparency of the composites is significantly increased by the presence of the silica shell on the doped QDs. This increase in transparency is not only due to the adjustment of the RI of the nanoparticles, but also to an improvement in the dispersion of the doped QDs. As shown in Fig. 2a and Fig. S4, aggregation of the doped QDs is effectively reduced by the addition of the silica shell, leading to a reduction in scattering. The thermal and UV stability of the doped ZnSe QD@SiO_2/epoxy composites were also tested (see Fig. S5 and S6). The PL of the composites becomes more stable after the nanoparticles are coated with the silica shell, which may result from protection of the doped ZnSe QDs from the outer environment by the silica shell.

A white LED was fabricated by combining the doped ZnSe QD@SiO_2/epoxy composite with a 365 nm UV LED chip. The doped QD layer exhibits much better transparency than that of the intrinsic QDs based white LED (see Fig. 4a and Fig. S7), with

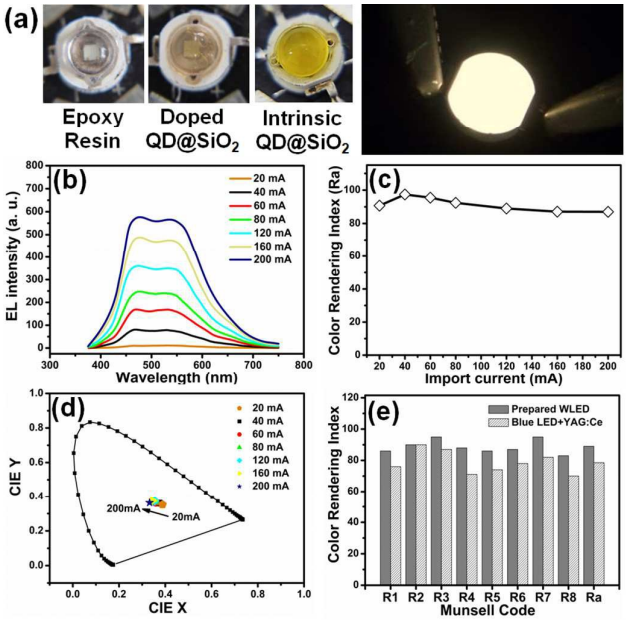

Fig. 4 (a) Images of LEDs based on pure epoxy encapsulation, doped ZnSe QD@SiO_2 NPs/epoxy encapsulation and intrinsic CdSe/CdS/ZnS QD@SiO_2/epoxy encapsulation; (b) EL spectra, (c) CRI values and (d) CIE color coordinates of the doped ZnSe QD@SiO_2/epoxy based WLED under different forward bias currents; (e) Munsell code of the doped ZnSe QD@SiO_2/epoxy based WLED operated at 120 mA.

bright white emission observed from the LED under 40 mA forward bias current. The electroluminescence (EL) spectra of the white LED operated at different forward bias currents from 20 mA to 200 mA were also measured (see Fig. 4b) and these spectra maintain a natural sunlight like spectrum under all forward bias currents. Due to the similarity of the emitted light to natural sunlight, the prepared WLED exhibited high CRI values (>85) under all tested forward bias currents (see Fig. 4c). When compared to YAG:Ce based commercial WLEDs (Ra~70), the doped ZnSe QD@SiO_2 nanocomposites based WLED gives higher values of Ra due to improvements of R4, R5, R6 and R7 corresponding to the color rendering of red and green (see Fig. 4e). This results from the ability to tailor different color components without reabsorption. Stable CIE (International Commission on Illumination or Commission Internationale de l'Eclairage) color coordinates (see Fig. 4d) were observed for all currents indicating good color stability of the output light. The maximum power efficiency (PE) of the WLED is 42.3 lm/W at 120 mA, which is significantly higher than common incandescent light bulbs (PE<18 lm/W) and higher than many reported WLEDs based on intrinsic QDs and blue LED chips[13, 21 22, 23]. The high fluorescence, stability, large Stokes shifts, and a device structure where most phosphors are far away from the LED chip accounts for the excellent device properties observed in this system. It is also worth noting that the use of doped ZnSe QD@SiO_2/epoxy transparent composites as light conversion and

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encapsulant materials may simplify the fabrication of WLEDs because it eliminates the need for a phosphor coating.

Conclusions

In summary, highly fluorescent Cu:ZnSe and Mn:ZnSe doped QDs were prepared via growth-doping and nucleation-doping strategies. The prepared QDs demonstrated strong emission under 365 nm UV light excitation, and exhibited enlarged Stokes shifts. No reabsorption was observed when the doped QDs with wavelengths of 470 nm, 550 nm and 605 nm were mixed, indicating they are ideal candidates for light conversion materials in WLEDs. The QDs were encapsulated in a silica shell through a reverse emulsion method in order to prevent aggregation of the QDs in the epoxy polymer as well as adjust the refractive index of the QD@SiO_2 nanocomposites. The mismatch between the refractive indices of the QDs and the epoxy resin was effectively reduced by 93% after silica encapsulation, resulting in transparent doped ZnSe QD@SiO_2/epoxy fluorescent composites. A WLED based on a UV LED chip in combination with the doped ZnSe QD@SiO_2/epoxy composite was fabricated, and showed high luminous efficiency and good color chromatics stability, indicating that these transparent fluorescent composites are promising light conversion and encapsulant materials for white-light sources for general lighting.

Acknowledgements

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