Abstract: In this research, we have developed an approach by incorporating quantum dots (QDs) with red emission into mesoporous silica microspheres through a non-chemical process and obtained luminescent microspheres (LMS). Owing to the lattice structure of LMS, QDs were effectively protected from intrinsic aggregation in matrix and surface deterioration by encapsulant, oxygen and moisture. The LMS composite has therefore maintained large extent luminescent properties of QDs, especially for the high quantum efficiency. Moreover, the fabricated white light emitting diode (WLED) utilizing LMS and YAG:Ce yellow phosphor has demonstrated excellent light performance with color coordinates around \((x = 0.33, y = 0.33)\), correlated color temperature between 5100 and 5500 K and color rendering index of Ra = 90, R9 = 95. The luminous efficiency of the WLED has reached up to a new record of 142.5 lm/W at 20 mA. LMS provide a promising way to practically apply QDs in lightings and displays with high efficiency as well as high stability.

Keywords: light emitting diodes, quantum dots, luminescent microspheres, color rendering index

1 Introduction

Colloidal quantum dots (QDs) have been developed as promising candidates for light converters in lightings and displays owing to their narrow emission band and tunable emission wavelength based on quantum size effects \([1–7]\). Specifically, the light quality, such as color rendering index (CRI), of traditional phosphor converted white light emitting diodes (pc-WLED) can be greatly improved by doping QDs with specific emission wavelength. In some typical cases, Sun’s group had employed different emission CdSe/CdS/ZnS QDs as light convertors in WLED obtaining Ra of 88 and luminous efficiency below 35 lm/W \([8]\). Later, the group had utilized red Cu: CdSQDs and yellow phosphors as light convertors in WLED and obtained high quality white light with CRI (Ra) and luminous efficiency reaching up to 86 and 40 lm/W at 20 mA, respectively \([9]\). Meanwhile, Aboulaich \textit{et al.} had also realized WLED with CRI (Ra) of 84 and luminous efficiency of 30.6 lm/W at 20 mA by employing YAG:Ce phosphors and red CuInS2 QDs as light convertors \([10]\). Moreover, Sohn \textit{et al.} \([11]\) and Kim \textit{et al.} \([12,13]\) had utilized bilayer structured QD-based light converting films to realize WLED with CRI (Ra) larger than 80 and luminous efficiency below 75 lm/W at 20 mA. The high performances were mainly contributed by the combination of various QDs or QDs and yellow phosphors, which composed the desired light converting material for the WLED.

However, these QD-optimized WLEDs would be severely challenged in practical applications due to their low luminous efficiency and worse stability. As nanoscale materials, QDs’ aggregation would be inevitably occurred inside the encapsulant, especially in high-temperature packaging process (e.g. silicone curing) resulting in the quench effect and consequent low conversion efficiency. The principle behind this phenomenon was mainly attributed to the incompatibility between the hydrophobic surface of QDs and encapsulant (e.g. silicone or polymers) \([14]\). Meanwhile, QDs with hydrophobic ligands...
are intrinsically sensitive to oxygen and moisture. These molecules could affect the bonding of ligands or etch the QDs’ surface, resulting in defect states [14, 15]. In practical cases, QDs’ composites have exhibited obvious decay on conversion efficiency in ambient circumstance, which was generally attributed to the surface damages [14]. In addition, the specific element Sulphur (S), existing in QDs’ inorganic surface and the organic layer, will seriously interfere with the curing of silicone by reacting with platinum (Pt) as a curing catalyst in most commercial silicones.

In order to functionalize QD materials and improve the stability of the composites, silica materials are widely utilized as QDs’ host matrix [14–19]. Meanwhile, epitaxial growth of composite layers (including QDs) on silica microspheres were also reported in Bawendi’s group [16, 17]. Moreover, in order to improve the stability QD-WLED, Jang et al. had developed a barrier layer formed by polyvinylpyrrolidone and silica on the composite film to protect QDs from photo-degradation [18]. The enhanced film-based WLED revealed excellent operational stability and the luminous efficiency reached up to 60 lm/W at 20 mA. However, such approach may not necessarily protect QDs from inner aggregation in polymer matrix. Additionally, the methods by growing silica layers on QDs’ surface before the LED packaging had been proved to be effective in composite stability. However, the growth process based on chemical surface engineering would severely damage the QDs’ surface, resulting in low luminous efficiency below 59 lm/W at 20 mA of final LED device [16, 18, 19].

In this work, novel silica-based luminescent microspheres (LMS) have been fabricated by incorporating red QDs into mesoporous silica microspheres (MS) with a non-chemical method. And the obtained LMS powders are utilized to improve the CRI (Ra) of pc-WLED with high luminous efficiency. The CdSe/ZnS QDs with red emission at 646 nm and absolute photoluminescence quantum yield (abs PL QY) up to 65% were synthesized according to our modified tri-n-octylphosphine (TOP) assisted successive ionic layer adsorption and reaction (SILAR) method [20]. And the method of incorporating QDs into MS was described as swelling and solvent evaporation. The similar strategy had been ever verified to be efficient in Sun’s group that incorporated QDs into Poly (styrene-co-maleic anhydride) particles to obtain low bio-toxic materials [21]. The as-prepared LMS were mixed with commercial YAG:Ce yellow phosphor as light converters in WLED. And the final WLED demonstrated excellent quality white light with optimized CRI characters (especially for Ra and R9 values) and remarkable high luminous efficiency even after high temperature curing process. LMS have shown great potentials to practically utilize QDs in LED devices with high efficiency and stability for lightings as well as displays.

2 Experiments

2.1 Synthesis of CdSe core

Highly fluorescent CdSe core QDs were prepared by a modified procedure from Hao et al. [20]. Typically, a mixture of 0.4 mmol of CdO and 3.2 mmol of stearic acid in a 50-ml three-neck flask was heated to about 220°C under an argon atmosphere to obtain a clear colorless solution. After cooling to room temperature, 50 mmol of octadecylamine (ODA) (ODA: Cd = 125:1) and 10 ml of octadecene (ODE) were added into the flask, and reheated to 270°C under argon atmosphere. After the heating device was removed, 4 mmol of Se in 4 ml of TOP was swiftly injected. The growth temperature was then reduced to 250°C for 6 min. Finally, the reaction mixture was cooled to room temperature, and an extraction procedure was used to purify the nanocrystals from side products and unreacted precursors. The obtained CdSe core was dispersed in n-hexane.

2.2 Preparation of the shell precursor solutions

The zinc precursor solution (0.1 mol/l) was prepared by dissolving ZnO (2 mmol) in 16 mmol of oleic acid and 15 ml of ODE at 290°C. The sulfur precursor (S-ODE) solution (0.1 mol/l) was prepared by dissolving sulfur in ODE at 130°C. All the precursors solutions were made under an argon atmosphere.

2.3 Synthesis of CdSe/ZnS core-shell QDs based on the TOP–SILAR method

High quality red CdSe/ZnS core/shell QDs was prepared by the modified TOP–SILAR method, which had been described in our previous research [20]. Typically, red CdSe QDs (2.7 × 10^{-5} mmol of particles) was dissolved in 5 ml of hexanes, then mixed with 1.6 g of ODA and 4.0 ml of ODE in a 50-ml three-neck flask. The flask was applied vacuum to remove hexanes with a mechanical pump at 70°C for 30 min, followed by removing any residual air from the system at 100°C for another 10 min. Subsequently, the sys-
High Efficiency and Color Rendering Quantum Dots

tem was switched to an argon atmosphere and the reaction mixture was heated to 140°C for the injections.

Then, 0.5 ml of TOP solution was injected as an activator, and the reaction mixture was further maintained at 210°C for 30 min. After the activation, 0.33 ml of Zinc precursor solution (0.1 mol/l) was injected and maintained at 200°C for 20 min. Then 0.33 ml of S precursor solution was added. The temperature was increased immediately to 220°C for 60 min to allow in-situ growth of the first ZnS monolayer. Cycling of injection and growth continued for the increased monolayers of ZnS shell, for instance, 40 ml of Zinc and S precursors is required for the growth of the second layer, and 48 ml for the third layer. The final product was diluted by hexanes followed by a methanol extraction. The extraction procedure was repeated for three times. The supernatant solution was further purified by centrifugation, and then dissolved in n-hexane for further use.

2.4 Preparation of LMS

As-prepared core-shell QDs (ca. 20 mg), after purification, and 100 mg of mesoporous silica powder with pore size of about 7 nm and diameter in 30–60 µm, purchased from Aladdin Reagent Co., Ltd., were dispersed in 20 ml n-hexane. The compound solvent was heated and maintained at 60°C with rapid stirring in an open single-neck flask for about 120 min with argon flow. During the heating process, solvent of n-hexane was intermittently injected into the flask in case of desertification before QDs incorporating into the silica lattice as much as possible. After the swelling process, the solvent was evaporated completely several times at the same temperature to obtain LMS powders.

2.5 Fabrication of WLEDs

For LMS-WLED, the prepared LMS powders (ca. 100 mg), YAG:Ce phosphors (160 mg), silicone 6550A (500 mg) and silicone 6550B (500 mg) were mixed in a 20 ml beaker to obtain a homogeneous latex. LMS–WLED was fabricated by dispensing the latex on an InGaN/GaN blue high power LED chip (50 × 50 mil) purchased from EPISTAR Corporation directly and then curing at 130°C for 30 min. Moreover, red phosphor-optimized WLED 1 and WLED 2 were fabricated in the same strategy with LMS–WLED but doping with 60 and 120 mg of red phosphors (SrCa)AlSiN3:Eu, respectively instead of LMS powders. Additionally, the bare WLED was also packaged in this method without adding any red emitters but just YAG:Ce yellow phosphors into the silicone 6550A and 6550B with the same ratio.

2.6 Characterizations

The absorptions were recorded by a UV-vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.). Photoluminescence (PL) spectra of as-prepared QDs were measured by fluroSENS spectrophotometer (GILDEN PHOTONICS). The abs PL QY values of QDs were confirmed by analyzing the ratio of the emitting photos to the absorbed photos in an integrating sphere accessory. High resolution transmission electron microscope (HRTEM) images were obtained on JEM-2100F transmission electron microscope. The electroluminescence (EL) spectra, Commission Internationale d’Eclairage (CIE) chromaticity coordinates, CRI values, Correlated Color Temperature (CCT) values and luminous efficiencies of the as-fabricated WLED were measured using an ATA-500 Spectral Radiation Analyzer (EVERFINE Corporation) with an integrating sphere at room temperature. The relative decays were determined by following formula

\[ \eta = \frac{P_{\text{final}}}{P_{\text{initial}}} \]

where P stands for light power and color subscripts indicate the wavelength ranges.

3 Results and discussion

Figure 1a–d show HRTEM images of as-prepared CdSe cores and CdSe/ZnS core-shell structured QDs in different resolutions. All the measured nanoparticles demonstrate uniform size distribution and clear lattice fringes that suggests monodispersed QDs with good crystallinity. Moreover, the HRTEM images suggest the average size of QDs has increased from 6.3 nm (bare CdSe core) to 6.8 nm (CdSe/ZnS core-shell), which were slightly smaller than that of pore size of the mesoporous silica powders and thus beneficial for QDs’ incorporating into swelled silica matrix.

The X-ray diffraction (XRD) pattern, as shown in Figure 1(e), confirms the lattice structure of the as-prepared QDs showing a cubic phase zinc blend structure. The lattice faces of (111), (220), and (311) are all observed to move towards larger angle (cubic ZnS phase), which indicates the successful inorganic coating of ZnS on CdSe [22]. Surface defects and dangling bands were therefore removed.
Figure 1: HRTEM image of as-prepared (a), (b) CdSe QDs, (c), (d) CdSe/ZnS QDs and (e) consequent XRD pattern on high resolution images. HRTEM: high resolution transmission electron microscope; XRD: X-ray diffraction.

efficiently, leading to the increase of abs PL QY value of the QDs [23].

Figure 2: (a) Absorption and PL spectra of as-prepared CdSe (blue line) and CdSe/ZnS (red line). (b) Schematic of the TOP-assisted SILAR method. PL: photoluminescence; TOP: tri-n-octylphosphine; SILAR: successive ionic layer adsorption and reaction.

Figure 2(a) illustrates the absorption and emission spectra of CdSe vs. CdSe/ZnS QDs. The apparent first exciton peaks from absorption curves and narrow emission peak widths (near 31 nm for FWHM) from PL spectra have confirmed the uniform size distribution of as-prepared QDs. In order to eliminate the surface defects more efficiently, TOP–SILAR method had been implemented to remove the surface lattice imperfections by the surface ions re-dissolution and lattice re-arrangement during the whole ZnS shell formation process. Figure 2(b) depicts the schematic of this efficient shell formation method. The surface imperfections, especially for surface lattice defects of core QDs, were consequently activated and removed by TOP solvent during inorganic epitaxial growth layer by layer, which was also beneficial for precisely controlling the ZnS growth. The abs PL QY was hence improved efficiently as shown in the PL spectra of Figure 2(a), from 41% (CdSe) to 65% (CdSe/ZnS). The abs PL QY values of QDs were confirmed by analyzing the ratio of the emitting photons to the absorbed photos with an integrating sphere system. Additionally, emitting centers of QDs were observed almost unchanged during inorganic coating process due to the steady size of CdSe core as the luminescence area [24].

Figure 3: Schematic of incorporation of QDs to obtain luminescent microsphere. QDs: quantum dots.

Figure 3 describes the schematic of SE method. After soaking and swelling treatment, the average pore size of silica powders was expected to be enlarged and thus beneficial for QDs’ embedding without any chemical treatment. Later, to improve the efficiency of QDs into MS, the QDs solution was then concentrated by solvent evaporation, which could force the QDs to penetrate the swelling pores and access inside the MS structure. Upon incorporation, the mesoporous structure could provide the network to prevent QDs’ aggregation improving the stability of QDs in MS matrix. More importantly, the structure reduced the contact surface between QDs and silicone encapsulant, consequently protecting the catalyst from invalidation and thus the silicone could solidify completely. Additionally, the lattice structure can also decrease the contact surface between QDs and permeated oxygen and moisture promoting their stability against surface deterioration.

Figure 4: (a) PL spectra of QDs in solution and LMS. (Inset: Photographs of the as-prepared QDs in solution and in microspheres) (b) Image of LMS by SEM. PL: photoluminescence; QDs: quantum dots; LMS: luminescent microspheres.
High Efficiency and Color Rendering Quantum Dots

PL spectra of QDs in solution vs. in MS are provided in Figure 4(a). A slight red shift is observed from the QDs in solution (646 nm) to those in MS (647 nm) due to the quantum states overlapping effect between closed QDs, which because of the physical separations between QDs become smaller during the SE process. Consequently, the reduction of abs PL QY from 65% in solution to 61% of QDs in MS can be also well explained by the overlapping quantum states of QDs in lattice work. Moreover, we can also recognize that the PL QY of LMS still keeps at a large extent of 93.8% comparing with that of QDs in solution, which indicates that the SE method is able to avoid damaging QDs’ surface caused by chemical surface engineering in traditional silica encapsulating process effectively.

Figure 5: (a) Schematic of LMS-optimized WLED. (b) As-fabricated WLED based on LMS and YAG:Ce phosphors. (c) LMS–WLED operating at 20 mA. LMS: luminescent microspheres; WLED: white light emitting diode.

To optimize white light quality, we have mixed LMS and YAG:Ce yellow phosphor as light converters in WLED. Figure 5(a) demonstrates the schematic of WLED packaging module with mixed phosphor and LMS on an InGaN/GaN blue LED chip. After rapid stirring, the obtained mixture showed homogeneous distribution of both yellow phosphor and red LMS particles in latex. Afterwards, a degassing process was taken before dispensing, by which the residual bubbles were thereby removed. Following the process of curing at 130°C for 30 min, the fabricated WLED device was ready for testing as shown in Figure 5(b). Comparing with QDs directly dispersing in silicone, the composite with the structure as QDs@MS@silicone could be well solidified and revealed high light conversion efficiency. Moreover, Figure 5(c) shows the WLED was lighted under a 20 mA current, revealing pretty high quality white light performance.

Operational performance on EL spectra, CIE color coordinates, luminous efficiencies, CCT and CRI values were all investigated under different currents. The results are given in Figure 6. EL spectra and CIE color coordinates of LMS-optimized WLED with increasing bias current from 20 to 200 mA are illustrated in Figure 6(a). A very slight shift of coordinates from (0.3394, 0.3418) at 20 mA to (0.3339, 0.3335) at 200 mA was observed, which revealed the high color stability and quality of the white light against the current variation in the WLED.

More importantly, excellent luminous efficiency, reaching up to 142.5 lm/W at 20 mA, was achieved, which is a new record of QD-optimized WLED from previous literatures [8–17, 23, 24]. And this is mainly contributed by the large number of survived high efficiency QDs in LMS after SE method and high temperature curing. Moreover, the luminous efficiency decreased for about 19% from 142.5 lm/W at 20 mA to 116 lm/W at 200 mA and the CCT consequently increased from 5203 to 5430 K as shown in Figure 6(b), which indicates the pretty good operational stability against currents alteration. Additionally, a significant improvement of CRI was also discovered by comparing LMS-optimized WLED with commercial pc-WLED in Figure 6(c). The Ra value, which refers to the average of R1 to R8 in different color area, has been improved from 76.8 to 90 for the LMS-optimized WLED vs. yellow phosphors-based WLED. More importantly, CRI R9 value has reached to 95 at 20 mA, indicating high performance of deep-red
Table 1: Light performance of as assembled WLEDs.

<table>
<thead>
<tr>
<th></th>
<th>Luminous efficiency (lm/W) @ 20 mA</th>
<th>CRI (Ra)</th>
<th>CRI (R9)</th>
<th>CCT (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QDs LMS–WLED</td>
<td>142.5</td>
<td>90</td>
<td>95</td>
<td>5171</td>
</tr>
<tr>
<td>Red-phosphor-WLED 1</td>
<td>128.6</td>
<td>87.6</td>
<td>62</td>
<td>5979</td>
</tr>
<tr>
<td>Red-phosphor-WLED 2</td>
<td>174.5</td>
<td>81.3</td>
<td>18</td>
<td>4624</td>
</tr>
<tr>
<td>Bare WLED</td>
<td>196.3</td>
<td>73.1</td>
<td>&lt;0</td>
<td>6134</td>
</tr>
</tbody>
</table>

LMS–WLED: luminescent microspheres-white light emitting diode; CRI: color rendering index; CCT: correlated color temperature.

Figure 7: (a) EL spectra of LMS–WLED, red phosphors-optimized WLEDs and bare WLED at 20 mA applied current. (b) Normalized decay curves of LMS–WLED and red phosphors-based WLED for accelerated ageing process at 85°C and 85% relative humidity. EL: electroluminescence; LMS-WLED: luminescent microspheres-white light emitting diode.

region. Light devices with higher R9 values can produce the most vivid colors due to that deep red is believed to be the key factor for accurately rendering colors of displayed objects. Additionally, from Figure 6(d), the color rendering stability against forward bias currents could be easily inferred.

In order to indicate the light performance and stability of LMS-WLED, we also assembled one bare yellow phosphor-based WLED (Blue chip and YAG:Ce yellow phosphor) and two red phosphors-optimized WLEDs (Blue LED chip, YAG:Ce yellow phosphors and red phosphors, (SrCa) AlSiN3:Eu, with emission wavelength at 623 nm) as comparisons, wherein WLED 1 possesses larger ratio of red phosphor to yellow phosphor than that of WLED 2. Figure 7(a) demonstrates the spectra of these WLEDs and their light performances can be found in Table 1. Though the bare WLED with YAG:Ce possesses the highest luminous efficiency reaching up to 196.3 lm/W at 20 mA, the R9 value was pretty low ascribing to the lack of deep red from the spectrum. Moreover, increasing ratio of red phosphor was helpful to promote the R9 value, from near 0 to 18 in WLED 1, but the promotion was still far away from the outstanding R9 performance. Meanwhile, the R9 value was further improved to 62 by increasing the ratio of red phosphors in WLED 2, however, the luminous efficiency was getting decreased to 128.6 lm/W because of broad emission of red phosphors costing too much luminous efficiency for light converting. We could draw a conclusion that though high CRI WLED could be achieved by utilizing more red phosphors, the luminous efficiency seemed difficult to maintain at high luminous efficiency level due to the broad emission of red phosphors. The LMS–WLED demonstrated not only excellent color rendering performance with Ra = 90 and R9 = 95, but also high luminous efficiency reaching up to 142.5 lm/W due to the narrow emission band and high quantum efficiency, which was greatly beneficial for obtaining specific emission wavelength, especially for R9 with less expending blue light power from the LED chip. Additionally, the decay curves illustrated in Figure 7(b) indicate the excellent stability of LMS in WLED, which is much close to that of high temperature sintered red phosphors, under a severe circumstance with high temperature (85°C) and high relative humidity (85% RH) for about 200 h.
4 Conclusion

In summary, QD-based LMS have been applied to fabricate the WLED with excellent performance in many aspects, for example, CIE color coordinates (0.3339, 0.3335), CCT between 5170 and 5430 K, and the highest luminous efficiency (up to 142.5 lm/W at 20 mA) among QD-optimized WLEDs in previous literatures to our best of knowledge. Such advantages are contributed by LMS that greatly maintain the PL properties of QDs as the LMS are prepared by a non-chemical method without surface deterioration of QDs, especially during the initial curing process under a high temperature. Furthermore, the mesoporous structures of LMS would help to prevent QDs from aggregation and photo-degradation, and therefore improve the compatibility between LMS and the LED encapsulant. Additionally, the red LMS could improve the color rendering properties of WLED, especially for the CRI R9 value up to 95 because of the high performance red QDs obtained from TOP-assisted SILAR method. LMS are believed to provide a promising way to practically apply QDs in lighting and displays with high efficiency as well as high stability.

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