Robust and Stable Narrow-Band Green Emitter: An Option for Advanced Wide-Color-Gamut Backlight Display

Xuejie Zhang,†,⊥ Hung-Chia Wang,†,‡ An-Cih Tang,‡ Shin-Ying Lin,† Hung-Chun Tong,‡ Ching-Yi Chen,‡ Yu-Chun Lee,‡ Tzong-Liang Tsai,¶ and Ru-Shi Liu*,†,§

†Department of Chemistry, National Taiwan University, Taipei 106, Taiwan
‡Lextar Electronic Corporation, Hsinchu 300, Taiwan
§Department of Mechanical Engineering and Graduate Institute of Manufacturing Technology, National Taipei University of Technology, Taipei 106, Taiwan

Supporting Information

White light-emitting diodes (LEDs) have already been widely used as backlighting components in modern liquid-crystal display (LCD). In this LCD display device, the color gamut is determined by the color coordinates of RGB emissions emitted from white LEDs passing through the corresponding RGB color filters.1–7 Apart from the InGaN-based blue LED chip, the luminescent properties (e.g., peak emission wavelength and full-width at half-maximum (FWHM)) of green and red emitters directly affect the space of the color gamut. In the state-of-the-art wide-gamut white LEDs, narrow-band green β-SiAlON:Eu²⁺ and narrow-band red K₂SiF₆:Mn⁴⁺ are considered optimum choices. The sharp red-emitting K₂SiF₆:Mn⁴⁺ phosphor with a peak at ∼630 nm is a classic luminescent material that is nearly ideal for phosphor-converted backlight white LEDs due to its merits including high external quantum yield and high color purity.8,9 The human eye has a high sensitivity toward the green spectral region; thus, green tones can be obviously distinguished. Presently, the narrowest green phosphor β-SiAlON:Eu²⁺ has a FWHM of 50 nm, which limits the maximum accessible color gamut of LCD.10 Thus far, a major challenge in backlighting LEDs is finding a narrower green emitter.

Recently, reports on perovskite CsPbBr₃ quantum dots (QDs) have been extensive.11,12 Perovskite CsPbBr₃ QDs are regarded as the most promising narrow-band green-emitting material used for wide-color-gamut backlight display because of their high photoluminescence quantum yields (PLQY), especially for their narrow-band emission with a FWHM of ∼20 nm.13–18 Despite their growing popularity, perovskite CsPbBr₃ QDs have widely recognized issues. First, the PLQY of CsPbBr₃ QDs was still hampered by the surface trap states. Second, the thermal stability of the current CsPbBr₃ QDs cannot handle the junction temperature of the operating LEDs. Third, the CsPbBr₃ QDs are easily degraded in humid environments or when exposed to water. In addition, the solution CsPbBr₃ QDs have widely recognized issues. First, the PLQY of CsPbBr₃ QDs was still hampered by the surface trap states. Second, the thermal stability of the current CsPbBr₃ QDs cannot handle the junction temperature of the operating LEDs. Third, the CsPbBr₃ QDs are easily degraded in humid environments or when exposed to water. In addition, the solution CsPbBr₃ QDs are unsuitable for direct use in on-chip white LEDs. To overcome these shortcomings, Pan et al.20,21 demonstrated a new method to improve the PLQY by introducing an inorganic–organic hybrid ion pair (didodecyl dimethylammonium sulfide, S²⁻–DDA⁺) to passivate the surface defects of QDs. To improve the thermal stability of CsPbBr₃ QDs, we22 provided a solution to mix green QDs with mesoporous silica particle. However, this mesoporous-CsPbBr₃ composite remains sensitive to water and oxygen. Using polymer coating is the simplest means to prevent the green CsPbBr₃ QDs from being exposed to water and further improve the stability of mesoporous-CsPbBr₃ powder. The compact polymer layer decreases the effect of oxygen and moisture because of the additional polymer coating on mesoporous-CsPbBr₃.

Taking inspiration from the above-mentioned treatments on CsPbBr₃ QDs to solve these acknowledged problems, we focused on exploring a robust and stable narrow-band green emitter for backlight display via the following three-step treatment presented in Scheme 1.

Scheme 1. Scheme of Three-Step Treatment on CsPbBr₃ Perovskite QDs through Didodecyl Dimethylammonium Sulfide Ion Pair (S²⁻–DDA⁺), Mesoporous Silica Particles, and Polymethylmetacrylate (PMMA)

Step 1: To obtain CsPbBr₃ QDs with high brightness, S²⁻–DDA⁺ was selected for passivation, which deals with the solution CsPbBr₃ QDs. The absolute PLQY of CsPbBr₃/SDDA could be further enhanced up to 80%.

Step 2: We mixed the solution CsPbBr₃/SDDA with mesoporous silica particle. The obtained powder mesoporous-CsPbBr₃/SDDA exhibited an obvious increase in thermal...
stability while the fwhm of the emission band remained constant.

Step 3: The mesoporous-CsPbBr3/SDDA was initially mixed with polymethylmetacrylate (PMMA). Then, we cured the mixture at 50 °C for 10 min. Peeled from the mold, the final mesoporous-CsPbBr3/SDDA@PMMA powder with isolating the water and oxygen was obtained.

After these three-step treatment, the mesoporous-CsPbBr3/SDDA@PMMA powder not only exhibited high PLQY and high thermal stability but also became a powder, similar to phosphor, with water resistance and narrow band. By employing red-emitting K2SiF6:Mn4+ and mesoporous-CsPbBr3/SDDA@PMMA powder, we fabricated a proof-of-concept white LEDs. After RGB emissions passed through the corresponding color filters, a wide-color-gamut up to 102% could be achieved. This value was larger than that when β-SiAlON:Eu2+ was used as the green emitter.

CsPbBr3 perovskite QDs were synthesized according to the reported hot-injection method. The details can be found in the Supporting Information. Figure 1a presents a structural overview of CsPbBr3 with cubic phase, illustrating a 3D framework of corner connected octahedral, with Cs+ occupying the cuboctahedral cavities in the framework. The powder X-ray diffraction (XRD) pattern in Figure 1b confirms the cubic phase of CsPbBr3 QDs. The morphology of CsPbBr3 QDs was detected using transmission electronic microscopy (TEM) (Figure 1c). These monodisperse QDs had cubic shapes with mean sizes of ∼10 nm. The high-resolution TEM (HR-TEM) image of the CsPbBr3 in Figure 1c also indicates the highly crystalline nature of the cubic phase CsPbBr3 with d-spacing of 5.8 Å. The absorption and emission spectra of solution CsPbBr3 QDs are shown in Figure 1d. The emission peak was centered at 514 nm with a fwhm of 21 nm under 460 nm excitation. We also measured the decay curve of CsPbBr3 QDs in toluene (inset of Figure 1d), which yielded a lifetime of 6.6 ns. The absolute PLQY of solution CsPbBr3 QDs was measured to be 45% with an excitation wavelength of 460 nm, which was not adequately enough because of the existence of surface defects.

To improve the absolute PLQY of perovskite CsPbBr3 QDs, we chose an inorganic−organic hybrid ion pair (S2−−DDA+) to passivate the surface defects in solution CsPbBr3 QDs. After optimization, the absolute PLQY of solution CsPbBr3/SDDA QDs reached 80% when a 50 μL sulfer precursor was added. The absolute PLQY of the treated sample improved by 77.8% compared with that of the untreated sample, indicates a better passivation of the surface trap states. The mechanism is that the ligand exchange process was occurred by replacing the native oleate functional group by the hybrid ion pair.20,21 The lifetime of CsPbBr3/SDDA QDs was 13.7 ns (Figure S1, Supporting Information), which is longer than that of CsPbBr3 QDs. This result is in accordance with the enhanced absolute PLQY due to the longer lifetime means better emitting property. The emission spectra of the untreated and treated samples are shown in Figure 2. Both the emission peak and fwhm of the two samples remained almost constant. The addition of the sulfer precursor in CsPbBr3 QDs only performed passivation to enhance the emission intensity and almost did not affect the structure of the QDs.

The poor thermal stability of CsPbBr3 QDs also impedes its practical and commercial application in on-chip LEDs. In this study, we mixed high brightness CsPbBr3/SDDA with purchased mesoporous silica particles. This mesoporous silica nanoparticles have an average size of 200−500 nm with pore size was approximately 12−14 nm. They provide adequate space where CsPbBr3/SDDA can be attached through physisorption. After this treatment, the emission peak shifted from 514 to 524 nm, whereas the fwhm remain almost unaltered. This red shift was acribed to the aggregation effect of QDs nanoparticles. The unchanged fwhm also indicates that the structure of CsPbBr3/SDDA was not damaged during the integration of mesoporous silica nanoparticles. The thermal stability of mesoporous-CsPbBr3/SDDA was expected to be improved because the mesoporous silica nanoparticles serve as a "protective shell". The thermal stability of CsPbBr3 and mesoporous-CsPbBr3/SDDA were compared (Figure 3a). As the temperature increased from 25 to 100 °C, the emission intensity of both samples decreased. At 100 °C, the emission

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Figure 1. (a) Crystal structure of cubic CsPbBr3; (b) XRD pattern of CsPbBr3 QDs; (c) TEM and HR-TEM of CsPbBr3 QDs; (d) Absorption and PL spectra of solution CsPbBr3 QDs; the inset shows the decay curve of solution CsPbBr3 QDs.
The intensity of mesoporous-CsPbBr₃/SDDA is 55% of the initial intensity at 25 °C, whereas the emission intensity of CsPbBr₃ decreased from 100% at 25 °C to 10% at 100 °C. This result indicates that the mesoporous-CsPbBr₃/SDDA powder sample exhibited better thermal stability than the solution CsPbBr₃ QDs. Moreover, the obtained mesoporous-CsPbBr₃/SDDA powder still had a high absolute PLQY of 71%.

To improve thermal stability further and protect the mesoporous-CsPbBr₃/SDDA against the air and moisture, we mixed mesoporous-CsPbBr₃/SDDA with PMMA and cured the mixture at 50 °C for 10 min. Then, the mesoporous-CsPbBr₃/SDDA@PMMA powder was obtained. The emission spectrum of mesoporous-CsPbBr₃/SDDA@PMMA is presented in Figure 2. By adding mesoporous-CsPbBr₃/SDDA into PMMA, the emission profile and emission peak wavelength of mesoporous-CsPbBr₃/SDDA@PMMA are nearly the same as those of the untreated sample, indicating that this treatment does not influence on the luminescence properties of mesoporous-CsPbBr₃/SDDA. The thermal stability of the final product mesoporous-CsPbBr₃/SDDA@PMMA was also investigated (Figure 3a). As expected, mesoporous-CsPbBr₃/SDDA@PMMA exhibited a more robust thermal stability than untreated mesoporous-CsPbBr₃/SDDA because of the polymer, which functions as a protective layer to isolate moisture and air. Thus far, the thermal stability has been improved from 10% at 100 °C (CsPbBr₃) to 65% at 100 °C (mesoporous-CsPbBr₃/SDDA@PMMA). The thermal cycling test also studied (Figure 3b). Although it underwent temperature cycling, mesoporous-CsPbBr₃/SDDA@PMMA exhibited high thermal stability because its intensity was nearly similar to that of the untreated CsPbBr₃ sample. During the package of white LEDs, the powder sample was more suitable than the solution sample. The obtained mesoporous-CsPbBr₃/SDDA@PMMA could play the role as the phosphor used in backlighting.

To demonstrate the potential application of mesoporous-CsPbBr₃/SDDA@PMMA, we fabricated white LEDs based on mesoporous-CsPbBr₃/SDDA@PMMA and K₂SiF₆:Mn⁴⁺ phosphor. The reason for choosing K₂SiF₆:Mn⁴⁺ is that this material exhibited an emission pattern consisting of several sharp lines (fwhm < 5 nm) at approximately 630 nm, which generates a 98.8% high color purity. Narrow-band green-emitting β-SiAlON:Eu²⁺ phosphor was also chosen as a comparison. The emission spectra of mesoporous-CsPbBr₃/SDDA@PMMA and β-SiAlON:Eu²⁺ are shown in Figure 4a. The fwhm of mesoporous-CsPbBr₃/SDDA@PMMA is narrower than that of the state-of-the-art β-SiAlON:Eu²⁺. In this study, we defined the white LEDs based on β-SiAlON:Eu²⁺ as phosphor white LEDs, whereas the white LEDs based on mesoporous-CsPbBr₃/SDDA@PMMA were defined as QDs-phosphor white LEDs. The color coordinates of phosphor and QDs-phosphor white LEDs were optimized at (0.264, 0.232) and (0.271, 0.232), respectively, in CIE 1931. Almost the same color coordinates benefitted when the color gamut of the two types white LEDs was compared. The electroluminescence spectra of the two types white LEDs are presented in Figure 4b.
For phosphor white LEDs, the emission wavelengths of RGB were 630, 527, and 458 nm (Figure 4b), corresponding to K$_2$SiF$_6$:Mn$^{4+}$, $\beta$-SiAlON:Eu$^{2+}$, and the blue LED chip. When passing through the color filters (conventional commercial products), the color coordinates of RGB were (0.675, 0.308), (0.231, 0.631), and (0.138, 0.066). These color coordinates generate a triangle area, that is, a color gamut, which overlapped with the NTSC space at approximately 89%. In comparison, the emission wavelengths of RGB in QDs-phosphor white LEDs were 630, 523, and 458 nm (Figure 4b). The respective color coordinates of RGB were (0.681, 0.305), (0.179, 0.683), and (0.140, 0.071) after the white LEDs passed through the same color filters. The color gamut was calculated to be approximately 102% of NTSC space, which was larger than phosphor white LEDs. The enhanced color gamut are contributing from the narrower-band green-emitting mesoporous-CsPbBr$_3$/SDDA@PMMA powder.

In summary, we presented a three-step treatment of perovskite CsPbBr$_3$ QDs toward high brightness and stable narrow-band green emitter. After the treatment, a robust and stable narrow-band perovskite mesoporous-CsPbBr$_3$/SDDA@PMMA powder was obtained. The powder exhibited several advantages, including a high absolute PLQY of 63%, a higher thermal stability, and good water resistance. Moreover, it could be easily used as a phosphor in packaging. Here, we mixed the narrow-band green-emitting mesoporous-CsPbBr$_3$/SDDA@PMMA powder and red phosphor K$_2$SiF$_6$:Mn$^{4+}$ in silicone and then packed it on the surface of a blue LED chip. A proof-of-concept white LEDs used in backlight display was successfully fabricated with color coordinates of (0.271, 0.232) that passed through RGB color filters with a NTSC value of 102%. All the results demonstrate the title green emitter based on perovskite CsPbBr$_3$ QDs is an option for advanced wide-color-gamut backlight display.

**ASSOCIATED CONTENT**

 Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.6b04107.

  - Experimental details; decay curve; water-resistance test (PDF)

**AUTHOR INFORMATION**

Corresponding Author
*Ru-Shi Liu. E-mail: rsliu@ntu.edu.tw. Tel.: +886-2-33661169. Fax: +886-2-33668671.

Author Contributions
$\n\$These authors contributed equally to this work.

Notes
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the Ministry of Science and Technology of Taiwan (Contract No. MOST 104-2113-M-002-012-MY3) and the Lextar Electronic Corporation.

**REFERENCES**


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**Figure 4.** (a) PL spectra of $\beta$-SiAlON:Eu$^{2+}$ phosphor and mesoporous-CsPbBr$_3$/SDDA@PMMA powder. (b) EL spectra of two white LEDs employing $\beta$-SiAlON:Eu$^{2+}$ phosphor and mesoporous-CsPbBr$_3$/SDDA@PMMA powder. (c) Color gamut of two white LEDs employing $\beta$-SiAlON:Eu$^{2+}$ phosphor and mesoporous-CsPbBr$_3$/SDDA@PMMA powder, and NTSC.