

CsPbBr₃ Embedded Cs₄PbBr₆ Nanocrystals for the Application in Electroluminescent Emitters and Mini LEDs

Ru-Shi Liu

rslu@ntu.edu.tw

Department of Chemistry and Advanced Research Center of Green Materials Science and Technology,
National Taiwan University, Taipei 106, Taiwan

Keywords: CsPbBr₃; Cs₄PbBr₆; perovskite; electroluminescent emitter, mini LEDs

ABSTRACT

Zero-dimensional perovskite-based nanocrystals (NCs) of CsPbBr₃ embedded Cs₄PbBr₆ (CsPbBr₃@Cs₄PbBr₆) are becoming the most attractive material due to their excellent optical performance and better stability compared with high-dimensional perovskites. The as-synthesized CsPbBr₃@Cs₄PbBr₆ NCs can be used to fabricate quantum dot light-emitting diode (QLED) devices and mini LEDs.

1 Introduction

Because of their excellent optical properties, such as narrowband emission,¹ high photoluminescence quantum yield (PLQY),² and better stability than three-dimensional perovskite, zero-dimensional perovskite Cs₄PbX₆ (X = Cl, Br, I) nanocrystals (NCs) have been considered as promising materials for applications in LEDs.

In this work, we successfully achieved high-quality CsPbBr₃@Cs₄PbBr₆ NCs by tuning the synthesis process of the hot-injection method. The as-synthesized CsPbBr₃@Cs₄PbBr₆ NCs were applied to fabricate QLED devices, which reached the best performance of all CsPbBr₃@Cs₄PbBr₆-system QLED devices. However, the synthesis of large-scale CsPbBr₃@Cs₄PbBr₆ complex nanocrystals (NCs) is difficult, and their application in mini- or micro-LEDs remains limited. Herein, we applied a microfluidic system for a simple, continuous, and stable synthesis of CsPbBr₃@Cs₄PbBr₆ NCs. The CsPbBr₃@Cs₄PbBr₆ complex NCs with uniform particles were obtained after the optimization of the Cs/Pb precursor ratio and alkaline environment and their photoluminescent quantum yield is up to 86.9%. These as-synthesized CsPbBr₃@Cs₄PbBr₆ NCs were used to produce a luminescent ink with the optimization of different solvents. This ink was successfully used to print large and high-resolution patterns and fabricated mini-sized color-converted LEDs. The narrow green emission of the LED well obeyed the requirements of the Rec. 2020 standard, demonstrating the potential of this material in the inkjet printing applications of color-converted mini- or micro-LED arrays.

2 Experiment

The following chemicals were used without purification: cesium carbonate (Cs₂CO₃, Aldrich, 99.9%), lead bromide (PbBr₂, ABCR, 98%), tin(II) bromide (SnBr₂, Alfa, 99.2%),

1-octadecene (ODE, Aldrich, 90%), oleic acid (OA, Sigma-Aldrich, 90%), oleylamine (OAm, Acros Organics, 80%–90%), and poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-sec-butylphenyl) diphenylamine))] (TFB; American Dye Source, Inc.). The substrates were commercial indium tin oxide (ITO) glass with a sheet resistance of 25 Ω/sq.

Exactly 400 mg of Cs₂CO₃ and 15 mL of ODE were mixed in a 50 mL three-necked flask, heated to 120 °C, degassed, and dried in a vacuum at 120 °C for 1 h. After degassing, 1.5 mL of OA was injected into the mixed solution. The temperature was then increased to 125 °C under an N₂ environment until all of the Cs₂CO₃ had reacted with OA. The Cs-oleate precursor solution was stored in a three-necked flask under N₂ until the synthesis of perovskite NCs.

Exactly 5 mL of ODE, 13.94 mg of PbBr₂, 41.77 mg of SnBr₂, 0.5 mL of OA, and 0.5 mL of OAm were mixed in a 50 mL three-necked bottle. Water and oxygen were removed under a vacuum for 30 min at 120 °C, after which the temperature was increased to 155 °C under an N₂ environment. The temperature was maintained at 155 °C for 10 min. Afterward, 0.6 mL of the Cs-oleate precursor that had been pre-heated to 120 °C was injected into the solution. After 5 s, the three-necked flask was placed in an ice bath and cooled to room temperature. The crude solution was subsequently centrifuged at 8000 rpm and 15 °C. The precipitate was dispersed in a hexane solution (about 10 mg/mL) to fabricate quantum dot light-emitting diodes (QLEDs).

QLEDs were fabricated on an ITO glass substrate which was cleaned with water and acetone under ultrasonication and ultraviolet (UV) ozone for 30 min. PEDOT:PSS was spin-coated at 3000 rpm for 45 s onto the ITO glass substrate and heated at 150 °C for 20 min to obtain a hole injection layer. TFB was spin-coated at 4000 rpm for 45 s and heated to 120 °C for 20 min. The CsPbBr₃@Cs₄PbBr₆ NCs solution was spun-cast onto the TFB layer at 1500 rpm for 45 s to obtain an emitting layer. After spin coating, TPBi (40 nm), LiF (2 nm), and aluminum (150 nm) were thermally deposited onto the QD emitting layer at 5 × 10⁻⁴ Pa. The overlapping area of the ITO and aluminum electrodes was approximately 2 × 2 mm².

The microfluidic system we applied in this work.

Before the synthesis, the inlet pipes of peristaltic pumps were wet into both precursors' bottles first. The precursors will be drawn into the microfluidic system at the same time with different floating ratios according to the program. The Cs–OA and the Pb–Br precursors were preheated in two heaters at 120 °C and 180 °C for more than 5 minutes before mixing with a T-mixer. The mixed hot solution immediately passed through a reactor at 180 °C to simulate the reaction temperature and the status of the hot injection process. After 1 minute, the solution floated out of the reactor, and the product was collected. After the synthesis, the remained precursors were pumped out by ODE to clear up the pipes of the microfluidic system. The collected product was centrifugated at 8000 rpm for 6 min to remove the solvent. Then the precipitate was dissolved in hexane with a concentration of 20 mg/mL for storage. The approximate amount of daily (24 h) production can go up to 432 mL such concentrated samples.

3 Results and Discussion

Transmission electron microscope (TEM) image of the optimized CsPbBr₃@Cs₄PbBr₆ NC ink as shown in Fig. 1a. The edges of CsPbBr₃@Cs₄PbBr₆ particles turned to be sleek, and there existed some dark dots in the particles. Thereby, we selected a big single CsPbBr₃/Cs₄PbBr₆ NC particle (about 46 nm, much larger than the average size), which can stand longer under the concentrated electron beam, to catch the high-resolution transmission electron microscopic (HRTEM) image. As we can see in Fig. 1b, a set of lattice fringes with a *d*-spacing of 0.67 nm was recognized to be the (-120) lattice plane of Cs₄PbBr₆. To find out the evidence of the embedded CsPbBr₃ particles, selected area electron diffraction (SAED) was also measured on this CsPbBr₃@Cs₄PbBr₆ NC particle (Fig. 1c). The bright rectangular patterns array in this image could be easily indexed as the lattice planes of Cs₄PbBr₆, proving the Cs₄PbBr₆ was well crystallized. Besides, a few weak diffraction patterns, which belong to the (002) and (011) planes of CsPbBr₃, were found within the gap of that rectangular array. This result further proved that the CsPbBr₃@Cs₄PbBr₆ NCs obtained in this work also have the structure of embedded CsPbBr₃ in the Cs₄PbBr₆ NC host. The absorption, photoluminescence (PL) excitation (PLE), and PL were checked in detail in Fig. 1d. These CsPbBr₃@Cs₄PbBr₆ NCs emitted a green emission at 514 nm with a narrow full width at half a maximum of 22 nm when excited by the 450 nm blue source. The PLE spectrum monitored at 514 nm showed it could be well excited at the wide range from ultraviolet (350 nm) to visible (510 nm). An excitation gap corresponding to the strong absorption peak appeared at around 315 nm, which belonged to the Cs₄PbBr₆ crystals. The absorption edge around 520 nm was too weak to be seen, indicating the quantity of CsPbBr₃ NC impurities decreased to a low level. Moreover, the PL decay times of these CsPbBr₃@Cs₄PbBr₆ NCs and CsPbBr₃ NCs were

measured (Fig. 1e).

Further study on the QLED was conducted to explore the future application potential of CsPbBr₃@Cs₄PbBr₆ NCs in high-quality displays. The typical structure of indium tin oxide (ITO)/PEDOT:PSS/TFB/CsPbBr₃@Cs₄PbBr₆ NCs/TPBi/LiF/Al was selected to fabricate the QLED device, as shown in Fig. 2a. The EL spectrum of the device at a working voltage of 4 V is shown in Fig. 2b. Compared with the PL spectrum, the EL emission peak redshifted 9 nm from 506 nm to 515 nm and keeps a narrow FWHM of 22 nm. The corresponding color coordinates of the PL and EL spectra in CIE are shifted from (0.053, 0.612) to (0.098, 0.738). In terms of the device's properties, the current density of the device continues to increase with the voltage up to 8 V, as shown in Fig. 2c, which proves the good conductivity of this device. Moreover, with the increase in voltage, the luminance of the device starts to increase from 2.7 V and reaches the maximum intensity of 1462 cd/m² at 6.2 V. Fig. 2d presents the EQE–current density curve and CE–current density curve of the applied QLED device. The highest EQE and CE of the device can reach up to 1.74% and 4.89 cd/A, respectively.

4 Conclusions

CsPbBr₃ Embedded Cs₄PbBr₆ (CsPbBr₃@Cs₄PbBr₆) NCs for the Application in Electroluminescent Emitters and Mini LEDs have been demonstrated.

5 Acknowledgements

This work was financially supported by the Advanced Research Center of Green Materials Science and Technology from the Featured Area Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education and the Ministry of Science and Technology in Taiwan.

References

- [1] Q. A. Akkerman, A. L. Abdelhady and L. Manna, "Zero-dimensional cesium lead halides: history, properties, and challenges," *J. Phys. Chem. Lett.*, Vol. 9, pp. 2326-2337 (2018).
- [2] Y. M. Chen, Y. Zhou, Q. Zhao, J.-Y. Zhang, J.-P. Ma, T.-T. Xuan, S.-Q. Guo, Z.-J. Yong, J. Wang and Y. Kuroiwa, "Cs₄PbBr₆/CsPbBr₃ perovskite composites with near-unity luminescence quantum yield: large-scale synthesis, luminescence and formation mechanism, and white light-emitting diode application. *ACS Appl. Mater. Interfaces*, Vol. 10, pp. 15905–15912 (2018).
- [3] Z. Bao, J. W. Luo, Y. S. Wang, T. C. Hu, S. Y. Tsai, Y. T. Tsai, H. C. Wang, F. H. Chen, Y. C. Lee, T. L. Tsai, R. J. Chung and R. S. Liu, "Microfluidic synthesis of CsPbBr₃/Cs₄PbBr₆ nanocrystals for inkjet printing of mini-LEDs," *Chem. Eng. J.*, Vol. 426, pp. 130849 (2021).

- [4] Z. Bao, H. D. Chiu, W. G. Wang, Q. Su, T. Yamada, Y. C. Chang, S. M. Chen, Y. Kanemitsu, R. J. Chung, and R. S. Liu, "Highly Luminescent CsPbBr₃@Cs₄PbBr₆ Nanocrystals and Their Application in Electroluminescent Emitters," *J. Phys. Chem. Lett.*, Vol. 11, pp. 10196–10202 (2020).

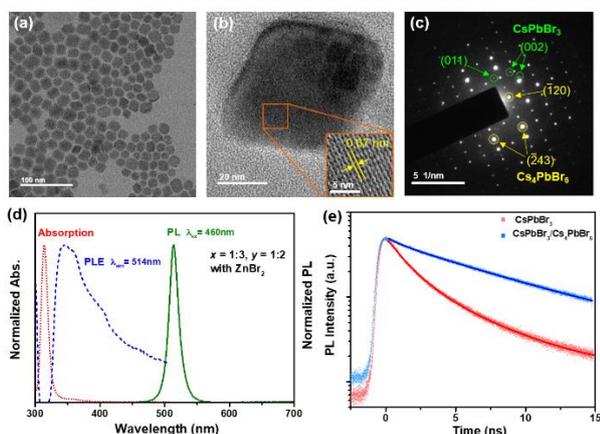


Fig. 1 (a) TEM image of the optimized CsPbBr₃@Cs₄PbBr₆ NC ink. (b) HRTEM image of a single CsPbBr₃@Cs₄PbBr₆ NC particle and (c) its SAED image. The planes of Cs₄PbBr₆ are indexed in yellow and those of CsPbBr₃ are indexed in green. (d) Absorption and PL spectra of the optimized CsPbBr₃@Cs₄PbBr₆ NC ink. (e) The PL decay curve of the optimized CsPbBr₃@Cs₄PbBr₆ NCs ink and CsPbBr₃ NCs synthesized without the additive ZnBr₂.^[3]

EQE–current density curve and CE–current density curve of the applied QLED device.^[4]

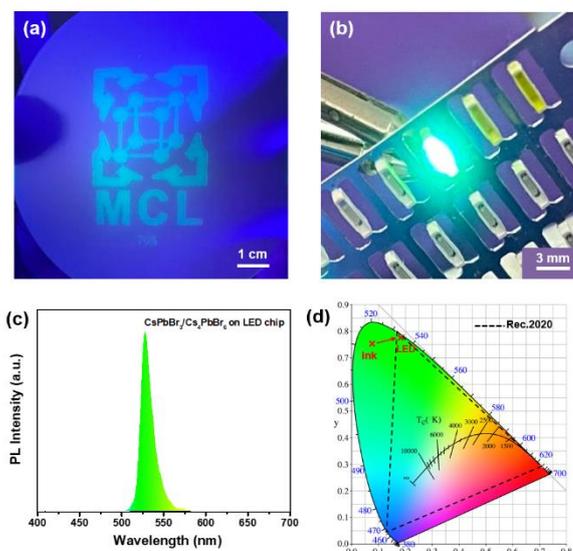


Fig. 3 (a) A photograph of the Materials Chemistry Laboratory (MCL) logo pattern printed by the CsPbBr₃@Cs₄PbBr₆ ink under UV light. (b) A photograph of the LED devices fabricated with CsPbBr₃@Cs₄PbBr₆ NC ink under working status and (c) their photoluminescent spectrum. (d) The color coordinate shift of the green emission in the LEDs compared with that of the original CsPbBr₃@Cs₄PbBr₆ NC ink. The dashed line triangle is the standard of Rec.2020.^[3]

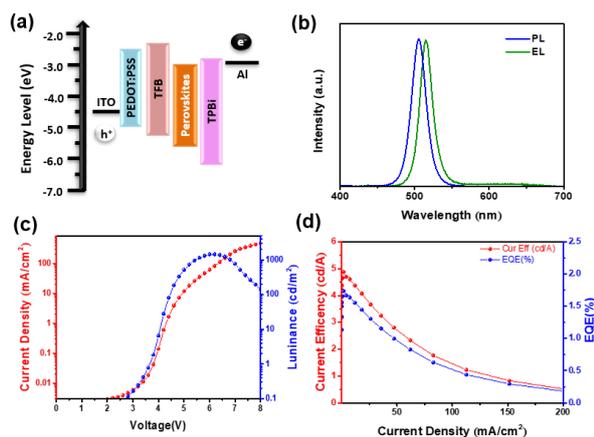


Fig. 2 (a) Structure and energy level alignment of the QLED device. (b) EL spectrum of the applied QLED device. (c) Luminance–voltage curve and current density–voltage curve of the applied QLED device. (d)