Efficiency Enhancement of Perovskite CsPbBr₃ Quantum Dot Light-emitting Diodes by Doped Hole Transport Layer

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Abstract: Balanced charge injection is essential to high-performance Perovskite CsPbBr₃ quantum dot-based light-emitting diodes (QLEDs). However, low mobility of hole-transport materials (HTMs) severely restrict improving performance of QLEDs. Herein, we provide a novel HTMs to improve the highest occupied molecular orbital (HOMO) energy level structure and carrier mobility by doping poly (9-vinylcarbazole) (PVK) and poly [N, N’-bis(4-butylphenyl)-N, N’-bis(phenyl) benzi-dine] (poly-TPD). We also introduce poly (methyl methacrylate) (PMMA) as electron block layer to further achieve charge injection balance. Finally, an enhanced external quantum efficiency (EQE) of 0.53% and 414.83 cd/m² was obtained. Compared with the untreated QLED, this result has been 8-fold enhanced, provides a new approach to attain better performance.

1. Introduction
In the field of optoelectronics, all-inorganic perovskite (CsPbX₃, X=Cl, Br, I) light-emitting diodes (LEDs) based on quantum dots (QDs) have become a central issue for their solution processability, low cost, high luminous efficiency and narrow emission spectrum. [1, 2] The LEDs based on CsPbBr₃ QDs was first reported to have an external quantum efficiency (EQE) of 0.035% [3], opening a new path for their application in optoelectronic devices. To improve the property of QLEDs, their emission mechanism should be better understood, and the influencing factors of EQE is as below: [4]

\[
\text{EQE} = \eta_{\text{out}} \cdot r \cdot q \cdot \gamma
\]  

(1)

Where \( \eta_{\text{out}} \) represents the optical coupling factor, which is generally less than 0.2. \( r \) represents the part of the radiation attenuation and \( q \) represents the PLQY of the emitter. \( \gamma \) reflects the charge balance, and generally a large \( \gamma \) attributes to more balanced charge injection. In recent studies, PLQY has been upgraded to over 90% [5], which is difficult to make further improvements. The effective optical coupling could improve the EQE of perovskite QLEDs, [6] but it is complicated to deal with the refractive index of each layer. The balance of carrier injection has been confirmed to improve the efficiency of LED due to the \( \gamma \) approaching to 1. However, there has been less study carrying on this method to balance charge injection. [7]

Generally, the architecture of perovskite CsPbBr₃ QLEDs is Cathode / Hole Injection Layer (HIL) / Hole Transport Layer (HTL) / Emitting Layer / Electron Transport Layer (ETL) / Electron Injection Layer (EIL) / Anode [8]. The perovskite CsPbBr₃ QLEDs can be roughly divided into four types according to the transport layer materials: QLEDs based on polymer charge transport layers, QLEDs exploiting small molecule charge transport layers, QLEDs with inorganic charge transport layers and QLEDs using hybrid transport layer. [9] In early researches, the commonly used charge transport
material was PVK[2], but the mobility of PVK was only $10^{-7}$ to $10^{-6}$ cm$^2$/Vs [10]. However, the mobility of the electron transport materials was much higher than PVK, making it difficult to balance the charge injection. Later, poly-TPD began to be used as hole transport material due to its higher carrier mobility [11], but the carrier mobility of poly-TPD was still lower than that of electron transport layer materials. Therefore, it has been a major challenge to develop high-efficiency all-inorganic perovskite CsPbBr$_3$ QLEDs via employing a better material as hole transport layer.

In addition, the traditional perovskite CsPbBr$_3$ QDs using oleic acid-oleylamine as a ligand has terrible conductivity because of the insulating property of oleic acid and oleylamine. Zeng reported a method to address the issue via ligand density control. [5] Wu replaced the ligand of oleic acid-oleylamine with DDAB by ligand exchange. [12]

The purpose of this study is to enhance the device performance of all-inorganic perovskite CsPbBr$_3$ QLEDs with a hybrid hole transport material doping PVK and poly-TPD, which can improve hole mobility and balance charge injection. An electron blocking layer employing poly (methyl methacrylate) (PMMA) is also introduced to limit the charge injection of electron transport layer. Compared with the LED using poly-TPD as hole transport layer, an 8-fold enhanced EQE of 0.53% is successfully achieved.

2. Experimental

2.1 Chemicals

Oleic acid (OA, 90%), 1-octadecene (ODE, 90%), oleylamine (OLA, 80%-90%), Lead (II) bromide powder (PbBr$_2$) and Cesium carbonate (Cs$_2$CO$_3$) were purchased from Sigma Aldrin. Didodecyldimethylammonium Bromide (DDAB), poly (3,4-ethylenedioxythiophene) polystyrene) solution (PEDOT:PSS, Clevis P VP Al 4083), Poly-TPD, PVK and PMMA were purchased from Xian Polymer Light Technology.

2.2 Synthesis of CsPbBr$_3$ QDs

The CsPbBr$_3$ QDs were synthesized following the reported procedures. [12] 15 mL of 1-octadecene (ODE), 2 mL of Oleic acid (OA) and 0.4 g of Cesium carbonate (Cs$_2$CO$_3$) were mixed in a flask. After 10 min under flowing N$_2$, the flask was heated to 120 °C as Cs-oleate precursor. Meanwhile, 10 mL of ODE and 0.138 g Lead (II) bromide powder (PbBr$_2$) were loaded to another flask, heated to 120 °C under N$_2$ flow. After 30 min, 1 mL OLA with 0.046 g of DDAB dissolved and 1 mL OA were added into the flask with PbBr$_2$. When the solute was dissolved, the flask was heated to 160 °C for 10 min and 0.8 mL of Cs-oleate precursor was quickly injected into it. After 5 s, the flask was dipped in ice-water to cool down. For purification, firstly, the crude solution was centrifuged at 10000 rpm for 6 min, and then the precipitate was dissolved in a mixture of toluene and ethyl acetate (1:2 v/v). The solution was centrifuged at 10000 rpm for 6 min again. The final product was diluted by n-hexane to 20 mg/mL.

2.3 Device fabrication

Firstly, ITO-coated glass was cleaned in water, acetone, isopropyl alcohol for 10 min respectively and treated with UV-ozone for 15 min. PEDOT:PSS (filtered through a 0.22 μm filter) was spin-coated onto the cleaned ITO-coated glass substrates at 3000 rpm for 40 s and annealed in air for 15 min at 120 °C. Hole injection material film was carried out in a glove-box, via spin-coating the material solutions with concentration of 8 mg mL$^{-1}$ at 3000 rpm for 40 s, and annealed for 15 min at 80 °C. The CsPbBr$_3$ QDs were deposited by spin coating at 2000 rpm for 40 s and PMMA solution were deposited by spin coating at 4500 rpm for 30 s. Tmppyb and Al/LiF were deposited in a vacuum deposition clamber.

2.4 Characterization

PL characteristics and absorption spectra were measured via Cary Eclipse spectrometer and Cary 50 UV-visible spectrophotometer respectively. Gemini SEM 500 system was used to record SEM images. UPS date were measured by a PREVAC system. JEOL JEM 2100 was utilized to record TEM images and HRTEM images.
3. Results and discussion

CsPbBr₃ QDs was synthesis following the method described above. Figure 1 (a) shows exciton absorption and photoluminescence (PL) emission of CsPbBr₃. Its absorption peak was located at 504 nm and the excitation peak was at 512 nm with the full width at half maximum (FWHM) of 18 nm. Low FWHM means uniform size of the nanocrystals. From TEM and HRTEM images in Figure 1 (b), cubic phase was confirmed with CsPbBr₃ QDs account for the lattice constants of 5.8 Å, 5.8 Å and 5.8 Å. Figure 1 (c) shows the SEM image of the CsPbBr₃ QDs film deposited by spin-coating displaying a the smooth surface, indicating that the size of CsPbBr₃ nanocrystal is uniform, which is beneficial to improve the film formation of the upper layer.

QLEDs with conventional HTMs obtain worse performance because of unbalanced charge injection, which limit EQE of QLEDs account for a great deal of nonradiative recombination. PVK and poly-TPD were doped in different proportions and then applied in LEDs as HTL. As shown in Figure 2 (a), the optimal doping ratio of poly-TPD and PVK is 1:4, achieving the maximum EQE of 0.33%. Moreover, the performance of QLEDs with PMMA of different concentration were also investigated. From Figure 2 (b) and Figure 2 (c), in contrast to the untreated QLEDs with the EQE of 0.07%, the QLEDs with PMMA of 0.16 mg/mL attain a maximum EQE of 0.53% and a brightness of 414.86 cd/m². The complete architecture used for the current study is shown schematically in Figure 3 (a), QLEDs use architecture of ITO (150nm) / PEDOT: PSS (40nm) / HTL (30nm) / CsPbBr₃ (30nm) / PMMA / Tmppyb (40nm) / LiF / Al (80nm). And the cross-sectional SEM image in Figure 3 (b) shows multiple layers of the LED, in which the PMMA layer and the LiF layer are indistinguishable, because of their low thickness.

![Figure 1](image1.png)

Figure 1. (a) UV–vis absorption and PL spectra, (b) TEM and HRTEM image of DDAB-CsPbBr₃ QDs, (c) SEM image of the surface of DDAB-CsPbBr₃ QDs film.
Figure 2. CsPbBr₃ QLED performance: (a) The highest EQE of different doping ratios (poly-TPD: PVK), (b) EQE of device with different PMMA concentrations, (c) Brightness of device with different PMMA concentrations.

The conventional HTMs are not conducive to hole transport due to the improper HOMO. From Figure 4 (a), UPS of different HTMs were tested to explain the reason for efficiency improvement. The results show that the HOMO energy level of poly-TPD and PVK is respectively 5.4 eV and 5.8 eV, while the HOMO energy level of hybrid HTMs is 5.51 eV, between the energy levels of PEDOT: PSS and CsPbBr₃, indicating an easier hole migration process. In addition, the carrier mobility of HTMs were measured and shown in Table 1. The carrier mobility of poly-TPD: PVK=1:4 is ~3.39E-03 m²/v.s, which is higher than others, because doped semiconductors can produce more majority carriers to accelerate recombination of majority carriers and minority carriers. Therefore, QLEDs with treated HTL shows better optical performance account for higher hole mobility approaching electron mobility could increase the radiation recombination of hole and electron in the emitting layer to improve EQE. Then, the current density of QLEDs with electron blocking layers added to the structure was measured. Figure 4 (b) shows that QLEDs utilizing PMMA of 0.16 mg/mL obtain significantly reduced current density, demonstrating the blocking effect of PMMA on electron transport.
Figure 3. (a) Structure diagram of the device, (b) SEM image of cross section of QLED.

We believe that the blocking effect of PMMA on the current leads to the balanced injection of hole and electron, improved the radiation recombination of carriers in the emitting layer. Because EQE of QLEDs first increases and then decreases as the concentration of PMMA increases, which indicates that the mobilities of hole and electron reach equilibrium in this process. The reduction of EQE could be attributed to the broken carriers balance due to further enhanced blocking effect of PMMA.

Figure 4. (a) the HOMO of materials measured by UPS. (b) Current density comparison of devices with or without PMMA.

Table 1. Carrier mobility of materials with different doping ratios obtained by Hall Effect Measurement System

| Sample No. | Poly-TPD:PVK | Carrier mobility [m^2/v.s] |
|------------|--------------|----------------------------|
| 1          | ∞            | -1.72E-05                  |
| 2          | 1:1          | -4.17E-04                  |
| 3          | 1:2          | -5.45E-04                  |
| 4          | 1:4          | -3.39E-03                  |
| 5          | 0            | -3.50E-06                  |

4. Conclusion
In this study, we adopt a novel method to enhance efficiency of CsPbBr₃ QLEDs by using hybrid HTMs
as HTL and PMMA to block electron. HTL doped with PVK and poly-TPD, under the synergistic action of PMMA, balances the carrier mobility in the emitting layer, furtherly improves the radiation recombination of exciton and the EQE of QLEDs. The mixture of PVK and poly-TPD shows more suitable mobility properties for LEDs with the doping ratio of 1:4. Moreover, a small amount of PMMA blocks the injection of electrons and balance charge injection. A high brightness of 414.83 cd/m² and EQE of 0.53%, which is increased by 8-fold compared to the untreated QLED is achieved.

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