Interfacial Engineering of Perovskite Quantum-Dot Light-Emitting Devices Using Alkyl Ammonium Salt Layer

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Herein, we demonstrated that alkyl ammonium salts containing the Br anion, oleylamine bromide (OAM-Br), was used as an interfacial engineering layer between the hole transport layer (HTL) and the perovskite QDs to passivate cation- and anion-defects in perovskite QDs. The OAM-Br interfacial layer enables a high PLQY due to the suppression of surface defects in perovskite QDs. Thus, the CsPbBr$_3$ QD-LEDs with an OAM-Br layer exhibited a maximum power efficiency of 3.35 lm/W and an external quantum efficiency (EQE) of 2.08% that which are higher efficiencies than those of the LEDs without an OAM-Br layer.

Keywords: Perovskites, Quantum dot, Light-emitting device, Interfacial engineering, Alkyl ammonium layer

1. Introduction

Recently, lead halide perovskites have received much attention for applications in solar cells [1], lasing [2], photodetectors [3], and light-emitting diodes (LEDs) [4-22] due to their narrow full width at half maximum (FWHM), electroluminescence emission tunable optical-band gaps, and easy of solution processability. Within a year since Tan et al.’s first report on organic-inorganic hybrid perovskite LEDs with green emission [4], the external quantum efficiency (EQE) was rapidly improved from 0.73% [4] to 8.53% [5] through interfacial engineering of the bulk perovskite films, stoichiometric control, and nanograin optimization. Moreover, a high EQE of over 10% was achieved with red emissive perovskite LEDs in 2016 [6,7]. Nevertheless, there remain some issues such as limited stability in organic-inorganic hybrid perovskite LEDs [8].

All-inorganic CsPbX$_3$ ($X = \text{Cl, Br, or I}$) quantum-dots (QDs), are highly stable at room temperature under atmospheric conditions [9,10]. Moreover, the perovskite QD-LEDs exhibit excellent properties, such as high color purity due to their narrow FWHM electroluminescence emission, color tunability in the visible light range, and high photoluminescence quantum yields (PLQYs) in solution state (over 90%) [11-19]. However, the PLQYs of perovskite QD films are still very low due to the formation of halide anion or cation defects on the surface of the perovskite QDs [20], during the purification process with poor solvents for reprecipitation [21]. Therefore, perovskite QD-LEDs have a lower EQE compared to organic-inorganic hybrid perovskite QD-LEDs. To overcome these drawbacks, we previously demonstrated a ligand exchange using alkyl ligand with a Br anion and effective purification with an ester solvent for highly efficient LEDs (EQE of 8.73%) [19]. Moreover, Zu et al demonstrated an effective post-treatment using an amine polymer to passivate the surface defect of the perovskite QD films [22]. Herein, we demonstrate the effectiveness of a post-treatment that uses an alkyl ammonium salt containing a Br anion, oleylamine bromide (OAM-Br), as an interfacial layer between the hole transporting layer (HTL) and the perovskite QDs layer to simultaneously achieve a
high PLQY and efficiency in LEDs.

2. Experimental
2.1. Materials
Poly(3,4-ethylenedioxythiophene):poly-(styrene sulfonate) (PEDOT:PSS) was purchased from Clevios. Poly(4-butylphenyl-diphenyl-amine) (poly-TPD) was purchased from American Dye Source and was used as received. Tris-[1-phenyl-1H-benzimidazole] (TPBi) and lithium 8-quinolate (Liq) were purchased from e-Ray Optoelectronics Technology Co., Ltd., and used as received. All chemicals were purchased from Sigma-Aldrich, and were used untreated.

2.2. Synthesis and washing of CsPbBr3 QDs
The CsPbBr3 QDs were synthesized using a previously reported method [11]. Cesium carbonate (542 mg, 99.99%) was loaded into a 25 mL three-neck-flask along with octadecene (ODE) (20 mL, 90%) and oleic acid (OA) (1.66 mL, 90%). The mixed solution was dried at 120 °C for 1 h under N2 until Cs-oleate formed. ODE (100 mL), OA (10 mL), oleylamine (OAM) (10 mL, 90%), and PbBr2 (1.38 g, 99.99%) were loaded into a 250 mL three-neck-flask, dried under vacuum at 120 °C for 1 h, and then heated to 180 °C under N2 flow. The Cs-oleate solution in ODE was then quickly injected. After 5 s, the reaction mixture was cooled in an ice water bath. The crude solution was centrifuged at 12000 rpm for 5 min, and the precipitate was collected and dispersed in toluene. The toluene dispersion was centrifuged at 12000 rpm for 5 min, and the supernatant with a stable dispersion was collected. Butanol (BuOH) was added to the toluene dispersion in a volume ratio of 1.5:1. The BuOH and toluene mixture dispersion was centrifuged again at 12000 rpm at 5 min, and the precipitate was collected and re-dispersed in octane. The OAM-Br powder was synthesized using a previously reported method [14].

2.3. Characterization
Photoluminescence (PL) spectra were obtained using a HORIBA FluoroMax-2 luminescence spectrometer. PLQYs were obtained using a Hamamatsu C9920–01 integral sphere system. PL lifetime measurements were collected using a Hamamatsu C11367 Quantaurus-Tau. Ultraviolet-visible (UV–vis) absorption spectra were measured using a Shimadzu UV-3150 UV–visible–NIR spectrophotometer. X-ray photoelectron spectroscopy (XPS) was performed with a Thermo Fisher Scientific Theta probe.

2.4. Device fabrication
Indium tin oxide (ITO) substrates were cleaned by ultrasonic spin-cleaning with deionized water and then by UV–ozone treatment for 10 min. After the UV–ozone treatment, Nafion blended with PEDOT:PSS (1:4 v/v) were spin-coated onto ITO-coated glass substrate and annealed at 150 °C for 10 min resulting in a 40 nm thick layer. For the preparation of the HTL, poly-TPD was dissolved in chlorobenzene at a concentration of 4 mg/mL, spin-coated onto the HTL at 1000 rpm for 30 s, and annealed at 100 °C for 10 min resulting in a 20 nm thick layer. The alkyl ammonium salt OAM-Br layer was spin-coated onto the poly-TPD layer at 2000 rpm 20 s and annealed at 100 °C for 10 min. CsPbBr3 QDs were spin-coated onto the OAM-Br layer at 2000 rpm for 30 s in a N2-filled glovebox.

Fig. 1. Optical properties of CsPbBr3 QD films with and without OAM-Br (a) UV–vis absorption and PL spectra, (b) PL decay curves of CsPbBr3 QD films.
Other functional layers of TPBi (50 nm) as an electron-transport layer, Liq (1 nm) as an electron injection layer, and Al (100 nm) as an anode were deposited by thermal evaporation under high vacuum (~1 × 10⁻⁵ Pa). The active area of the device was 2 mm². The perovskite QD-LEDs were characterized after encapsulation using epoxy glue and a glass cover. Electroluminescence (EL) spectra were recorded using a Hamamatsu PMA-11 photonic multichannel analyzer. The current density voltage and luminance−voltage characteristics were measured using a Keithley source measure unit 2400 and a Minolta CS200 luminance meter, respectively.

3. Results and discussion

Figure 1a shows the UV-vis absorption and PL spectra of the perovskite QDs layers with and without the OAM-Br layer. The OAM-Br solution in methanol was prepared at a concentration of 10 and 15 mg/mL. All samples exhibited identical absorption and PL spectra, indicating that the OAM-Br interfacial layer does not affect the optical bandgap and peak wavelength. On the other hand, the PLQYs of the CsPbBr₃ QDs with OAM-Br layers were significantly improved from 35.9% (without OAM-Br) to over 70%, as shown in Table 1. The CsPbBr₃ QD films with OAM-Br layers prepared from 10 and 15 mg/mL solution exhibited high PLQYs of 68.0% and 72.2%, respectively. In order to better understand the relationship between OAM-Br and the PLQY, a PL lifetime analysis was performed; the result are shown in Fig. 1b. The PL decay of the CsPbBr₃ QD with an OAM-Br layer was slower (10-11 ns) than that of the CsPbBr₃ QD without an OAM-Br layer (9.6 ns), which strongly indicating that the suppression of non-radiative recombination [23].

We also performed an XPS survey of the high-resolution N 1s core-level spectra of CsPbBr₃ QDs with and without OAM-Br, as shown in Fig. 2. The XPS spectra of CsPbBr₃ QDs without OAM-Br showed two-component peaks, which corresponded to the protonated amine group (-NH₃⁺) at 401.8 eV and amine groups at 399.9 eV [24,25]. On the other hand, the peak corresponding to the amine groups (399.9 eV) for the CsPbBr₃ QDs with OAM-Br decreased in intensity with increasing peak intensity of the protonated amine groups (401.8 eV). This result showed that the CsPbBr₃ QDs were covered with protonated amine groups, which in turn indicated that the cation defects were passivated by the amine groups of the OAM-Br.

We fabricated CsPbBr₃ QD-LEDs with OAM-Br layers with the following structure; ITO (130 nm)/PEDOT:PSS blended with Nafion (20 nm)/poly-TPD (20 nm)/OAM-Br/CsPbBr₃ QDs/TPBi (50 nm)/Liq (1 nm)/Al anode (100 nm), as shown in Fig. 3a. The EL spectra, current density-voltage, and luminance-voltage characteristics of QD-LEDs are shown in Figs. 3b-d. Identical EL spectra were observed for the CsPbBr₃ QD-LEDs with and without OAM-Br. The QD-LED with OAM-Br exhibited a higher current efficiency of 5.29 cd/A at 100 cd/m² compared to the QD-LED without OAM-Br, which had a current efficiency of 0.74 cd/A at 100 cd/m². In addition, we achieved a remarkably higher power efficiency and EQE for the QD-LED with OAM-Br of 3.24 lm/W and 2.07% at 100 cd/m², respectively, as compared to those for the untreated CsPbBr₃ QD-LED (0.43 lm/W and 0.29% at 100 cd/m², respectively). This result indicated that the CsPbBr₃ QD-LEDs with an OAM-Br layer showed not only high PLQYs but also high EQEs owing to passivation of surface defects such as cation defect.

![Fig. 2. XPS of CsPbBr₃ QD films with and without OAM-Br.](image)

Table 1. Summary of the photophysical characteristics of the CsPbBr₃ QD films with and without OAM-Br.

| Amine layer          | PLQY (%) | PL peak (nm) | FWHM (nm) |
|----------------------|----------|--------------|-----------|
| w/o OAM-Br           | 35.9     | 512          | 19.7      |
| 10 mg/mL OAM-Br      | 68.0     | 513          | 19.4      |
| 15 mg/mL OAM-Br      | 72.2     | 512          | 19.7      |
4. Conclusion

In summary, we demonstrated the interfacial engineering effects of using alkyl ammonium salt OAM-Br for CsPbBr$_3$ QDs. The bilayer of OAM-Br/CsPbBr$_3$ QDs showed a high PLQY of 72.2% and an FWHM of 19.7 nm owing to passivation of the surface defects in CsPbBr$_3$ QDs. Using a simple post-treatment with an OAM-Br layer, a maximum power efficiency of 3.35 lm/W and an EQE of 2.08% could be achieved for the CsPbBr$_3$ QD-LEDs with OAM-Br.

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