Significance of Energy-Level Alignment in 3D Perovskite ELs

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Abstract

In this study, we report a significant phenomenon that EL performances for 3D materials, such as $CsPbX_3$, are governed by adjacent charge transport layers, which is possibly due to nonradiative recombination resulting from the small exciton binding energy. To overcome this issue, we developed a new electron transport layer (ETL) that enhances exciton confinement effect in 3D $CsPbX_3$. Consequently, we achieved ultra-high brightness of 500,000 cd/m^2 at a very small operating voltage of 5V.

1. Introduction

Metal halide perovskites, such as $CsPbX_3$ (X: I, Br and Cl), have emerged recently as a promising candidate for emission layer (EML) in EL device due to their promising optical properties, i.e., very narrow full width at half maximum (FWHM), and good compatibility for solution process [1]. $CsPbX_3$ is suitable for next generation display, printable LEDs made by spray coating and ink-jet printing. However, the performance of $CsPbX_3$-based ELs (PeLED) is still low compared to the conventional OLED. For commercialization of PeLED, low efficiency problem should be solved.

Recently, low-dimensional (Low-D) perovskite materials have attracted attention as a one of the solutions due to their high photoluminescent quantum yields (PLQY), which resulting from quantum confinement effect (QCE) [2]. However, it is unclear whether low-D materials with QCEs are superior to 3D materials for electroluminescent devices (EL). Generally, 3D and low-D materials possesses different intrinsic property in respect to exciton binding energy and charge transport properties as shown Figure 1a. Low-D materials exhibit poor charge transport nature because of their highly localized electronic structures. In the view of EL device, 3D material with good charge transportability is preferable to Low-D materials. However, small exciton binding energy issue of 3D material leading non-radiative recombination should be solved to exploit this characteristic to boost EL device performance.

EL devices, such as OLEDs is constructed by several functional layers including electron transport layer (ETL), the EML, and the hole transport layer (HTL), which is a two-dimensional architecture where an ETL and HTL confine the EML. Figure 1b shows ideal device structure between charge transport layer (ETL/HTL) and EML. If the ETL and HTL have the energy levels to sufficiently confine electrons and holes, the whole device structure can be considered as a scaled-up Low-D material. In other words, the conduction band minimum level (E_{CBM}) and valence band maximum level (E_{VBM}) of the ETL/HTL should be shallower and deeper than those of the EML, respectively. However, it is difficult to obtain ETL/HTL materials that satisfy both energy alignment and charge transportability.

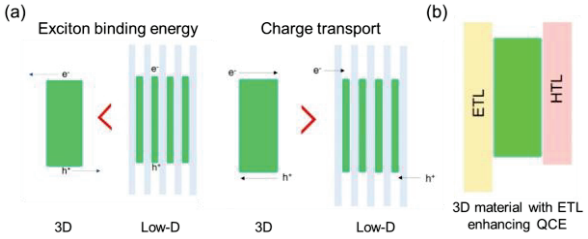

Figure 1. (a) Charge transport properties and exciton binding energy of 3D materials and Low-D materials. (b) Proposed ideal energy alignment of 3D materials with ETL or HTL.

In this work, we introduce a strategy to obtain the exciton confinement effect and good charge transport using a unique electron transport layer (ETL) material. The proposed amorphous oxide semiconductor, Zn-Si-O (a-ZSO) ETL material has sufficiently shallow electron affinity (~3.2 eV) to confine excitons and high electron mobility (~0.8 cm2/Vs) to transport electrons [3]. Furthermore, the tunable conductivity and electron affinity of a-ZSO enables fine-tuning of charge balance. As a result, a very low operating voltage of 2.9 V at 10,000 cd/m^2 and high efficiency of 33 lm/W were achieved for 3D $CsPbBr_3$ based green-PeLED. The obtained ultra-high brightness of ~500,000 cd/m^2 shows the effectiveness of our strategy for PeLEDs. We also extend this strategy into 3D $CsPbBrI_2$ (red) PeLEDs. As a result, the highest luminance and the lowest operating voltages of 20,000 cd/m^2 at 5 V. We believe this study provides a new insight into the realization of

practical PeLEDs.

2.1 Correlation between Exciton quenching of 3D $CsPbBr_3$ and energy level of adjacent layers

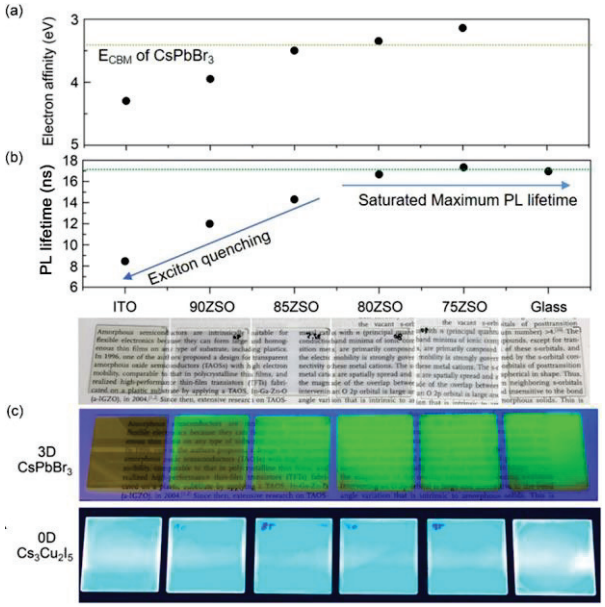

Figure 2. (a) Electron affinity values of ITO, 90ZSO, 85ZSO, 80ZSO, and 75ZSO. (b) PL lifetimes and photo of PL from $CsPbBr_3$ thin films fabricated on ITO, 90ZSO, 85ZSO, 80ZSO, 75ZSO, and bare glass substrates. (c) Photograph of $CsPbBr_3$ and $Cs_3Cu_2I_5$ thin films on each substrate under UV light excitation.

To evaluate how the energy alignment of $CsPbBr_3$ with neighboring layers affects PL property, we prepared several a-ZSO thin films of different Zn/(Zn+Si) ratio (90, 85, 80, and 75%) by depositing on glass substrates using RF magnetron sputtering at room temperature. $CsPbBr_3$ thin films were fabricated on each substrates by using spin coating. Figure 2a shows the energy levels of the relevant materials and Time-resolved PL spectra were measured and PL lifetimes were obtained from the PL decay curves. As shown in Figure 2b, a noticeable correlation was be confirmed between the energy alignments and PL lifetime. The $CsPbBr_3$ on ITO exhibited the shortest PL lifetime, which well agrees with the photograph (Figure 2c). On the other hand, PL lifetime increased and saturated at ~17 ns with increasing the ratio of Si in a-ZSO. This value (~17 ns) was almost the same with that of the sample deposited on bare glass substrate, which implies that the a-ZSO (Si ≥ 20%) possesses an suitable energy level to confine excitons in $CsPbBr_3$. The PL dependence of Low-D materials on the energy-level alignment with neighboring layers was estimated by using a zero-dimensional (0D) light emitting material, $Cs_3Cu_2I_5$ with very large exciton binding energy of ~ 490 meV [4]. All $Cs_3Cu_2I_5$ samples showed bright emission regardless of the neighboring layer (Figure 2d). These results clarify that the luminescent material with larger exciton binding energy is less sensitive to its neighboring layers.

2.2 Boosting EL performance and Significance of Charge balance in PeLED

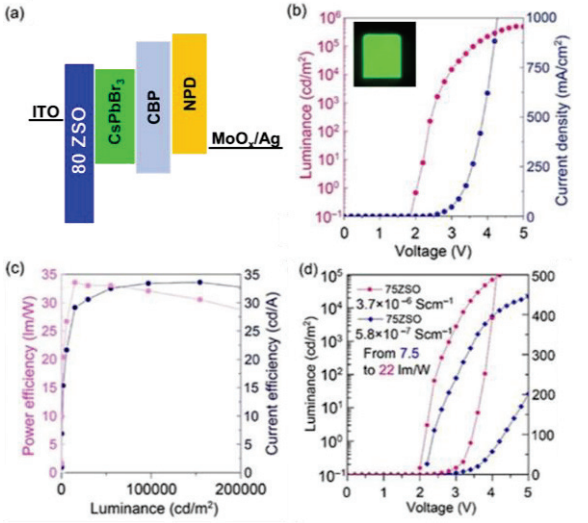

Figure 3. (a) The band alignment of PeLED with QCE. (b) Luminance–current density–voltage characteristic and (c) power efficiency (lm/W) and current efficiency (cd/A) of the PeLED with 80ZSO ETL. (d) EL performance of PeLEDs using 75ZSO ETLs with different conductivities.

In order to evaluate the ability of a-ZSO as an ETL, PeLED with 80ZSO was fabricated with the inverted structure (ITO (150 nm)/80ZSO (120 nm)/ $CsPbBr_3$ (60 nm)/CBP (20 nm)/NPD (20 nm)/MoOx (5 nm)/Ag (100 nm)). In the band alignment of PeLED as shown in Figure 3a, $CsPbBr_3$ was perfectly confined by 80ZSO and CBP as an ETL, HTL, respectively. As a result, $CsPbBr_3$-PeLED exhibited very low operating voltage, i.e., 10,000 cd/m^2 at 2.9 V and 500,000 cd/m^2 at 4.8V (Figure 3b), while high power efficiency of 33 lm/W were also achieved thanks to the low operating voltage (Figure 3c). This superior EL performance substantiates the success in effective charge injection to $CsPbBr_3$ and good charge balance. Furthermore, we performed conductivity fine-tuning of 75ZSO ETL in order to demonstrate the advantage of a-ZSO as ETL in PeLED. The conductivity of a-ZSO can be easily controlled by sputtering condition, such as partial oxygen pressure and RF power. As shown in Figure 3d, when changing the conductivity of 75ZSO from 5.8×10^{-7} to 3.7×10^{-6} Scm^{-1}, the operating voltage decreased and current density increased. Besides, the power efficiency increased from 7.5 to 22 lm/W. This shows that a transparent amorphous oxide semiconductor ETL, such as a-ZSO, has a merit to simply optimize the charge balance of EL device due to their

widely-tunable electrical properties.

2.3 High compatibility of 3D perovskite in PeLED using a-ZSO

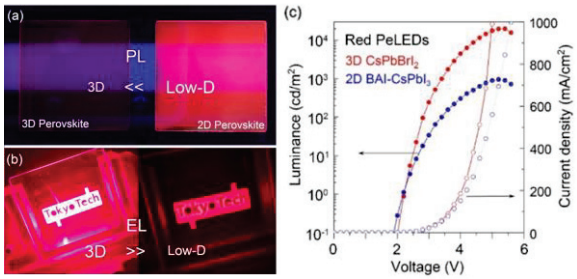

Figure 4. (a) Photographs of (a) PL and (b) EL for 3D $CsPbBrI_2$ and 2D BAI-$CsPbI_3$, respectively. (c) Luminance –current density–voltage (L–J–V) characteristics of the $CsPbBrI_2$ PeLED and the 2D BAI-$CsPbI_3$ PeLED.

To demonstrate the validity of our strategy, we fabricated red PeLEDs by using 3D $CsPbBrI_2$ and 2D BAI-$CsPbI_3$ [5] as an EML, respectively. PL property was also compared by fabricating each thin films on glass substrate. As shown Figure 4a, it was clearly confirmed that 2D BAI-$CsPbI_3$ exhibits much brighter red light than 3D $CsPbBrI_2$ under UV-light excitation. This result agrees well with recent report [5] and shows the low dimensionality definitely improves the brightness by QCE. However, EL performance was clearly contrary to the result of PL property. 3D $CsPbBrI_2$ PeLED showed much brighter EL performance than 2D red PeLED (Figure 4b). Very low operating voltage and high brightness were confirmed: 2.8 V for 100 cd/m^2, 3.4 V for 1,000 cd/m^2 and 4.5 V for 10,000 cd/m^2. (Figure 4c) To the best of our knowledge, the obtained maximum luminance of 20,000 cd/m^2 is the top value among the red PeLED recently reported. This result suggests that 3D material is more favorable than 2D material by using a-ZSO in PeLED.

3. Conclusion

We clearly proved that EL performances of 3D $CsPbX_3$ are governed by adjacent charge transport layers, which possibly result from the non-radiative recombination by the small exciton binding energy. The newly proposed a-ZSO ETLs enabled to improve the exciton confinement effect with utilizing the good charge transport nature of 3D CsPbX3. Consequently, ultra-high luminance with low operating voltages was realized for green and red PeLEDs. This study would provide a new direction into the accomplishment of practical PeLEDs.

4. References

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