High performance organo-lead halide perovskite light-emitting diodes via surface passivation of phenethylamine

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\textbf{ABSTRACT}
One of the organometal halide perovskite materials, i.e., methylammonium lead bromide (MAPbBr\textsubscript{3}), possesses interesting and incredible physicochemical properties, and shows great promising in light-emitting device. However, the poor morphology and high defect density properties of MAPbBr\textsubscript{3} films limit the performance of perovskite light-emitting diodes (PeLEDs). Here, high efficiency PeLEDs based on MAPbBr\textsubscript{3} is demonstrated by the incorporation of phenethylamine (PEA). We find that the introduction of PEA into the precursor of MAPbBr\textsubscript{3} reduces the grain size and increases the coverage of MAPbBr\textsubscript{3} films. In addition, it also passivates the surface defects of the grains, which all lead to high photoluminescence efficiency. In order to promote the charge injection into the MAPbBr\textsubscript{3} grains, suppress the exciton quenching at the interface of perovskite film and hole transporting layer (HTL)/electron transporting layer (ETL), the device structure of “insulator-perovskite-insulator” is employed to further improve the performance of the PeLEDs. Under optimized ratio of MA and PEA, a maximum current efficiency 9.81 cd A\textsuperscript{-1} is achieved. Our work presents an facile and robust route for high performance PeLEDs.

\textbf{1. Introduction}
Recently, organic–inorganic lead halide perovskite materials, with a three-dimensional ABX\textsubscript{3} structure (where A for methylammonium (CH\textsubscript{3}NH\textsubscript{3}+), MA or formamidinium (HC(NH\textsubscript{2})\textsubscript{2}+, FA) cation; B for Pb\textsuperscript{2+}, Sn\textsuperscript{2+} or Ge\textsuperscript{2+} metal ion; X for I\textsuperscript{-}, Br\textsuperscript{-}, Cl\textsuperscript{-} halide ion [1,2]), have attracted considerable interests in optoelectronic applications owing to their interesting and incredible physicochemical properties [3–5], such as facile solution process ability [6–9], balanced charge transport properties with long diffusion lengths [10,11], tunable band-gaps [12–14], high carrier mobilities [15–17], and low non-radiative recombination ascribed to their unique defect chemistry [18,19]. Moreover, the demonstration of high photoluminescence (PL) quantum efficiency in the hybrid perovskite suggests effective light emitters for light-emitting diodes, and the optical absorbance can be easily tuned across the entire visible spectrum via halogen substitutions [20–23].

Since the first realization of perovskite light-emitting diodes (PeLEDs) at room temperature pioneered by R. Friend and his coworkers in 2014 [24], organic–inorganic lead halide perovskite materials have been at the basis of several breakthroughs in the development of light-emitting devices. So far, H. Cho et al. overcame the electro-luminescence efficiency limitation of PeLEDs and made a breakthrough in current efficiency (CE) of the device up to 42.9 cd A\textsuperscript{-1} and external quantum efficiency (EQE) to 8.53% within only one year [25]. However, the efficiency of PeLEDs is intrinsically limited by poor coverage and big grains of the perovskite film directly prepared by a one-step spin-coating method from its pure precursor solution, resulting in serious non-radiative leakage current losses in the PeLEDs. So far, a number of approaches have been developed to overcome those problems. In the preparation process of perovskite thin films, anti-solvents such as chlorobenzene, toluene, and diethyl ether are used to control the formation process of the perovskite film to achieve a uniform and
smooth surface [26,27]. These interfacial treatments, however, are complex and delicate, which limits the reproducibility of the fabrication process of the perovskite film. In addition, two-step methods have been widely adopted to attain uniform perovskite films [28]. However, these methods could lead to reduced grain size and poor crystallinity of perovskite films, resulting in high defect density and thereby inferior luminescent properties. Therefore, preparation of smooth perovskite films with full coverage and passivation of the grain surface are still open problems to be solved for the high performance PeLEDs.

In this work, we introduce phenethylamine (PEA) into methylammonium lead bromide (MAPbBr₃) system to improve the performance of PeLEDs devices based on MAPbBr₃ thin film. PEA is found to effectively improve the coverage and passivate the surface defect of MAPbBr₃ film. By utilizing the device structure of “insulator-perovskite-insulator” that we developed recently, an efficient green emission with lumiance of 29268 cd m⁻² and the maximum current efficiency of 9.81 cd A⁻¹ with promising device stability can be achieved.

2. Experimental section

2.1. Perovskite precursor

A 38 wt% MAPbBr₃ perovskite precursor solutions (PbBr₂:MAPb molar ratio = 1:1.5) were prepared by dissolving PbBr₂ (Aldrich, 99.999%) and MAPb (Borun New Material Technology LTD) in anhydrous dimethylformamide (DMF), and then stirred at 60 °C for 2 h in a nitrogen-filled glove box. After that, 1 μL, 3 μL, 5 μL, 10 μL and 20 μL PEA solutions (Acros Organics, 99%) were separately added into 1 ml of the above-mentioned MAPbBr₃ precursor solutions in which the molar ratio = 1:1.5 were prepared by dissolving PbBr₂ (Aldrich, 99.999%) and MABr (Borun New Material Technology LTD) in anhydrous dimethylformamide (DMF), and then stirred at 60 °C for 2 h in a nitrogen-filled glove box. After that, 1 μL, 3 μL, 5 μL, 10 μL and 20 μL PEA solutions (Acros Organics, 99%) were separately added into 1 ml of the above-mentioned MAPbBr₃ precursor solutions in which the final volume ratios of PEA solution to MAPbBr₃ precursor solution is 0.1%, 0.3%, 0.5%, 1% and 2%, respectively. After stirring at 60 °C for 1 h in a nitrogen-filled glove box, the hybrid precursor solutions were obtained.

2.2. Fabrication of PeLEDs

Firstly, indium tin oxide (ITO) patterned glass substrates with sheet resistance of about 15 Ω/square were cleaned with deionized water and organic solvents, and then exposed to UV–ozone ambience for 5 min. Secondly, the substrates were transported into a vacuum chamber, and then 3 nm LiF (Sigma-Aldrich, 99.999%) layer was deposited onto the ITO-coated substrates via thermal evaporation under high vacuum (< 3 × 10⁻³ Pa) with the rate of about 0.2 Å/s monitored in situ by a quartz-crystal sensor. After deposition, the ITO/LiF substrates were transferred into a nitrogen-filled glove box in which the above-mentioned MAPbBr₃ precursor solutions were coated using a 3D MAPbBr₃ cluster is protected by long-chain PEA ions, which effectively improve the coverage and passivate the surface defect of MAPbBr₃ film. The discrete quantum level generated by this “quantum well” structure is reported to be more conducive to the selective carrier transport [5,29]. As shown in Fig. 1b, when no PEA is introduced, the perovskite film begins to in situ by utilizing the device structure of “insulator-perovskite-insulator” that we developed recently, an efficient green emission with lumiance of 29268 cd m⁻² and the maximum current efficiency of 9.81 cd A⁻¹ with promising device stability can be achieved.

3. Results and discussion

By using one-step solution process, the schematic diagram of the MAPbBr₃ structural change after PEA introduction is shown in Fig. 1a. In the (PEA) (MA)PbBr₃ perovskite, small fraction of three-dimensional (3D) MAPbBr₃ cluster is protected by long-chain PEA ions, which greatly improves the stability of the MAPbBr₃ crystal structure. The discrete quantum level generated by this “quantum well” structure is reported to be more conducive to the selective carrier transport [5,29]. As shown in Fig. 1b, the fabricated device by introducing different amounts of PEA into MAPbBr₃ precursor solution, and then spin-coating onto an indium tin oxide (ITO) substrate covered with a thin LiF layer followed by post-annealing (see Experimental Section).

The surface morphology and microstructure of the perovskite film have a critical impact on the performance parameters of the device. SEM images of MAPbBr₃ films fabricated with different amounts of PEA in MAPbBr₃ precursor solution is shown in Fig. 2a–f. As shown in Fig. 2a, when no PEA is introduced, the perovskite film with large grains and low surface coverage can be observed. When the PEA ratio increases to 0.1%, the surface coverage of MAPbBr₃ film begins to increase, though the grain size is not found to reduce, as shown in Fig. 2b. Furthermore, when the PEA ratio increases to 0.3%, the surface coverage of resultant film is significantly improved and the crystal size is relatively reduced as shown in Fig. 2c. While the PEA ratio exceeds 0.3%, the surface coverage of MAPbBr₃ film gradually increases as shown in Fig. 2d–f. As depicted, the surface coverage of the MAPbBr₃ film is significantly increased with increasing dosage of PEA, especially, the surface coverage reaches 100% when the dosage of PEA is more than 1%.

The crystallinity of the perovskite films is also verified by XRD. As
shown in Fig. 2g, the MAPbBr$_3$ films fabricated with different amounts of PEA show diffraction peaks at 14.9° and 30.03°, which can be assigned to (100) and (200) facets of a cubic perovskite structure, respectively [30,31]. Increasing of PEA dosage causes the decrement in peak intensity, and the peaks almost vanish for 2% of PEA dosage. This result demonstrates that the crystallinity of MAPbBr$_3$ perovskite crystal deteriorates, which can also be verified by SEM images. We speculated that the introduction of PEA into the perovskite precursor solution may suppress the crystal growth of MAPbBr$_3$ [32,33].

In order to further explore the role of PEA in the formation of the MAPbBr$_3$ crystal, optically pumped experiments were carried out to estimate the trap state density in the films. The MAPbBr$_3$ films with different amounts of PEA (0%, 0.3% and 1%) on glass substrates are excited at 400 nm by a frequency-doubled Ti:sapphire femtosecond laser oscillator delivering 150 fs pulses at a 1 kHz repetition rate.

Through a pinhole filter and a positive lens, the laser beam forms a 3 mm diameter spot and is irradiated obliquely onto the surface of the samples. Face emission spectra were collected directly into a fiber optic spectrometer. The measured output emission spectra and the input-output intensity of the samples as a function of increasing pump energy are shown in Fig. 3a–c. The first intersection represents the pump energy needed to fill all the traps (i.e., the threshold trap pump energy $P_{\text{trap}}$). As shown in Fig. 3, $P_{\text{trap}}$ of the MAPbBr$_3$ films with different amounts of PEA 0% (a), 0.3% (b) and 1% (c) are ~27, 14, and 11 μJ cm$^{-2}$, respectively, corresponding to the calculated trap state densities of $-6.37 \times 10^{17}$, $3.5 \times 10^{17}$, and $2.65 \times 10^{17}$ cm$^{-3}$, respectively. In addition, to further explore the trap state densities of PEA (0.3%) in the formation of the MAPbBr$_3$ films, the bulk defects and surface traps were estimated with a formula as follows [34]:

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**Fig. 2.** Top-view SEM images of MAPbBr$_3$ films fabricated with different volume PEA of 0% (a), 0.1% (b), 0.3% (c), 0.5% (d), 1% (e) and 2% (f), respectively. (g) XRD patterns of perovskite films prepared by different ratios of PEA.
where $n_{TP}$ is the trap states density, $a_i$ is the product of the trapping cross section and the carrier velocity, $k$ is a constant. The fitted values of bulk trap density and surface trap density is about $5.6 \times 10^{16}$ and $2.9 \times 10^{17}\text{cm}^{-3}$, respectively, as shown in Fig. 3d. Obviously, the introduction of appropriate ratio of PEA (0.3%) could effectively improve the film quality, reduce the trap state density and lower the bulk trap density in the MAPbBr$_3$ films, and greatly improve the corresponding device performance. Although the introduction of excessive PEA further leads to lower trap density, in turn, the introduction of excess ligands molecules impairs the charge carrier transport and injection to the perovskite active layer, and has negative effects on the device, leading to a poor device performance.

The relationship between the emission properties and the perovskite film structures is studied using steady-state PL spectra, as shown in Fig. 4a. It is observed that the PL peaks have similar positions in all perovskite films with different amounts of PEA. The PL peaks of all perovskite films shift from $\lambda \approx 533\text{nm}$ to $\lambda \approx 528\text{nm}$ with increasing amounts of PEA. The blue-shift of PL spectra is attributed to the amine group of PEA, which results from the change of crystalline structure, film morphology, and the surface trap passivation effect [35]. As shown in Fig. 4a, the PL intensity elevated as the dosage of PEA increased. This increase in PL intensity can clearly be attributed to the surface coverage improvement of MAPbBr$_3$ films. As PEA is an insulating molecule, it will make short circuiting blockage in different layers across the active layer and confine the injected electrons and holes into the active layer for the radiative recombination, which causes the increase in PL intensity. However, excess introduction of PEA molecules, which impairs the charge carrier transport and injection to the perovskite active layer, negatively affects the performance of devices.

To further understand the photoelectric properties of these films, PL lifetime is estimated additionally, as shown in Fig. 4b. PL lifetime of the MAPbBr$_3$ is considered as the summation of quick and moderate decay components. The quick decay is identified with trap-associated recombination at grain limits, which is commonly known as a non-radiative process, though the slow or moderate decay is identified with radiative recombination inside the grains. Typically, the shorter lifetime indicates the higher recombination rate [23]. As can be seen in Fig. 4b, the PL lifetime is gradually extended with the increased amounts of PEA. This result indicates that the treatment of MAPbBr$_3$ by amine group in PEA can significantly reduce non-radiative recombination rate by decreasing the defect density.

In order to achieve the high performance of the PeLED device, the structure of “insulator-perovskite-insulator (IPI)” were employed, where a pair of ultrathin LiF films were used as insulating layers shown in Fig. 5a. IPI-structured PeLEDs had been reported in our previous work [36]. A series of PeLEDs with different thickness of LiF insulated layers were prepared so as to get the ideal device structure in this work as shown in Fig. S1. The optimized thicknesses of LiF at the two interfaces are 3 nm and 8 nm, respectively, as shown in Fig. 5b. The ultrathin LiF films play two roles in devices, one is to induce carriers into perovskite crystals, improve their recombination and block the leakage current through the gaps or holes in perovskite films; the other is to avoid the exciton quenching at the interface between perovskite film and holes/electrons transport layer. From our previous report, the IPI-structured PeLEDs show the higher performance than that of conventional PeLEDs [36].

The luminance versus voltage (L–V) and current efficiency versus voltage characteristics of the devices are shown in Fig. 6a and b,
respectively, and the electroluminescent parameters are presented in Table 1. The turn-on voltage (while the luminance achieves 1 cd m\(^{-2}\)) of the films is around 3 V. This result shows the potential application in low driving voltage light-emitting devices. With a special structure and excellent MAPbBr\(_3\) film, the most noteworthy luminance of 29268 cd m\(^{-2}\) is achieved at a driving voltage of just 10.2 V, and the maximum current efficiency of 9.81 cd A\(^{-1}\) at 8.2 V in the 0.3% PEA devices. It is worth to note that EL peaks of the devices shifted from \(\lambda \approx 533\) nm to \(\lambda \approx 528\) nm with increasing the doping content as shown in Fig. 6d, which is in agreement with the PL spectra in all the cases.

To correlate the relationship between the morphology of the MAPbBr\(_3\) films and the performance of PeLEDs device, we further analyze the performance of the devices. The current efficiency of 3.3 cd A\(^{-1}\) is achieved in the 0% PEA devices. The low current efficiency is due to the large particles and great amount of pinholes, which also led to contact between ITO and Bphen, though a IPI structure is used. While after the introduction of 0.1% PEA in MAPbBr\(_3\), the number of pinholes reduces and the surface coverage improves, as evidenced in Fig. 2a. Because the MAPbBr\(_3\) film shows low coverage, the device still has a low current efficiency and luminance. Despite of this, the current injection still becomes easier compared to 0% PEA devices. When PEA increased to 0.3%, a maximum luminance of 29268 cd m\(^{-2}\) and a current efficiency of 9.81 cd A\(^{-1}\) can be obtained. The morphology of the MAPbBr\(_3\) film is significantly improved and the crystal size is relatively reduced, which makes current injection much easier. In addition, the amine group of PEA can passivate the surface of MAPbBr\(_3\) grains. Based on advanced IPI device structure, we obtained an efficient green emission PeLED with the most noteworthy luminance of 29268 cd m\(^{-2}\) and the maximum current efficiency of 9.81 cd A\(^{-1}\) in the 0.3% PEA devices. In addition, the introduction of PEA can also improve the stability of PeLEDs. Our work demonstrate a facile and robust method to increase coverage and reduce defect states of thin MAPbBr\(_3\) films, which will be of great significance for improving the performance of PeLEDs.

4. Conclusion

In summary, we have presented a facile one-step method to produce high current efficiency PeLEDs by introducing the PEA into MAPbBr\(_3\) system. It is found that the introduction of PEA favors the formation of smaller grains, increases the coverage of MAPbBr\(_3\) films, and also passivates the surface of MAPbBr\(_3\) grains. Based on advanced IPI device structure, we obtained an efficient green emission PeLED with the most noteworthy luminance of 29268 cd m\(^{-2}\) and the maximum current efficiency of 9.81 cd A\(^{-1}\) in the 0.3% PEA devices. In addition, the introduction of PEA can also improve the stability of PeLEDs. Our work demonstrate a facile and robust method to increase coverage and reduce defect states of thin MAPbBr\(_3\) films, which will be of great significance for improving the performance of PeLEDs.

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The properties of PeLEDs with different volume ratios of PEA.

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<th>PEA Volume ratio</th>
<th>EL Peak (nm)</th>
<th>PL Peak (nm)</th>
<th>CE (cd A⁻¹)</th>
<th>Luminance (cd m⁻²)</th>
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<td>533</td>
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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.orgel.2018.05.026.

References


