# Highly compact CsPbBr<sub>3</sub> perovskite film decorated by PEO for light-emitting diodes

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**Abstract:** Inorganic perovskite light-emitting diodes (PeLEDs) with full coverage and compact films were realized by doping a certain amount of PEO into perovskite emitting layer. The additive PEO (Polyethylene oxide) can not only improve the coverage of films by physically filling the pin-holes of crystal boundaries but also act as a protective layer to passivate the films, which successfully reduce the rate of non-radiative recombination, and enhance photoluminescence quantum yield (PLQY) of the CsPbBr<sub>3</sub> films. In addition, PEO can also decrease the surface roughness of the perovskite films. As a result, the addition of PEO can improve the transport capability of carriers in PeLEDs. By optimizing the concentration of PEO, a maximum external quantum efficiency (EQE) of 0.26% and brightness of 1432 cd/m<sup>2</sup> were achieved, which is significantly improved compared with previous work. The results presented in this paper shows that the additive PEO in perovskite precursor solution paves a new way for the application in PeLEDs.

## **1 INTRODUCTION**

In recent years, halide perovskite has attracted enormous attentions in the fields of solar cells and light-emitting diodes (LED) due to their excellent optical properties, including the high color purity, narrow spectrum width (full width at half maximum, FWHM  $\approx$  20 nm), high charge carrier mobility, and tunable color across the entire visible spectrum, which shows enormous potential to act as the new generation of lighting and displaying fields. Furthermore, solution-processed methods greatly lower the cost of the devices which is also easier for fabricating photoelectric devices. Most of the previous work mainly focus on the organic-inorganic hybrid perovskite (MAPbBr<sub>3</sub>) due to their remarkable widely-tunable performance such as emission wavelength (400-780 nm)<sup>[2-5]</sup>. Although the EQE of the MAPbBr<sub>3</sub>-based PeLEDs device has reached 9.3%<sup>[6]</sup>, the issue that MAPbBr<sub>3</sub> perovskite materials are extreme sensitive to moisture and heat still have not resolved, which greatly limits the application of MAPbBr<sub>3</sub> perovskite materials.

Comparatively, all-inorganic CsPbBr<sub>3</sub> based crystalline perovskite film has attracted great interest due to its great stability comparing with the organic-inorganic hybrid perovskite thin film. What's more the emission peak of CsPbBr<sub>3</sub> crystalline film located at around 520 nm, which is fully compatible with the super-pure green demand of the National Television System Committee (NTSC)<sup>[7-8]</sup>. Nevertheless, the CsPbBr<sub>3</sub>-based LED devices are facing several problems. The brightness and current efficiency of CsPbBr<sub>3</sub>-based LED are not as high as we expected, due to its low PLQY and poor coverage

of perovskite films, which can cause serious leakage of current<sup>[9]</sup>. Therefore, the way to improve the quality of the perovskite films plays a key role in achieving high brightness and efficiency of PeLEDs. Some researchers use the method to control the conditions of films formation process such as treatment with non-polar solvent<sup>[10]</sup>. However, this process is so complicated that greatly limits the repeatability. Reducing the pin-holes of the film by adding some additives such as PIP<sup>[11]</sup> is also used in some works. This is an effective strategy to suppress the non-radiative recombination of carrier, however, the performance of the CsPbBr3-based LED devices are still have not satisfied. As a result, an effective way to improve the coverage of perovskite films is urgently needed to obtain the PeLEDs with high brightness and efficiency.

In this paper, a small amount of PEO were doped into the CsPbBr<sub>3</sub> precursor solutions to get compact and pin-hole free perovskite films with small grain size. The coverage and the surface roughness of the films are measured by SEM and AFM. In addition, the mechanisms why the brightness and EQE of the PeLEDs are significantly improved are explained, which is different from the previous reports that only considered the coverage factor of the films<sup>[12]</sup>. The additive PEO can effectively improve the PLQY and suppressing the current loss. The EQE of PeLEDs with additive PEO is up to 0.26% and the brightness is up to 1432 cd/m<sup>2</sup>, which are several times than the devices without PEO.

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# 2 EXPERIMENTAL

#### 2.1 Materials

PbBr<sub>2</sub> and CsBr were purchased from Sigma Aldrin. PEDOT:PSS (poly (3,4-ethylenedioxythiophene) polystyrene) solution (Clevis P VP Al 4083) and TPBi were purchased from Xian Polymer Light Technology Corp. DMSO and PEO (Aw= 1,000,000) were purchase from Al fa Caesar. All these materials were used without further treatment.

#### 2.2 Synthesis of CsPbBr<sub>3</sub>-Based perovskite precursor solutions

CsBr and PbBr<sub>2</sub> were mixed at the molar ratios 1.5:1 in DMSO to obtain a concentration of 206 mg/ml precursor solution. Then three different concentrations of PEO solutions were parepared, 5 mg/ml, 10 mg/ml, 15 mg/ml respectively. These two kinds of solutions were stirred at  $70^{\circ}$ C for 6 hours and with the molar ratio of 1:1 before use.

> 1432 cd/m<sup>2</sup> and 0.26% respectively. CsPbBr3 in PEO in DMSO Precursor in DMSO solution solution solution ıbstrate r.m.s=34.8 nm (e) (f) r.m.s=27.1 nm 5mg/m (g) r.m.s=14.7 nm (h) r.m.s=96.9 nm 15mg/

Figure 1. The schematics about Preparation of perovskite precursor solution and the process of film spin coating followed by thermal annealing.

# **3 RESULTS AND DISCUSSION**

# 3.1 Characterization of perovskite films

Generally, the quality of the perovskite film is a very important factor to improve the performance of the photoelectric devices such as solar cells and light-emitting diodes. The poor performance of pure CsPbBr<sub>3</sub> in film forming makes it challenging to achieve high-quality CsPbBr<sub>3</sub> thin films. As a result, with substantial current leakage caused by incomplete surface coverage, the maximum brightness of PeLEDs based on CsPbBr3 thin films remains only 407 cd/m2 with peak EQE of 0.008%<sup>[1]</sup>.

In this work, we found that the addition of a small amount of PEO into the perovskite precursor solutions could obtain the smooth and pinholes free films with small crystal boundaries and less pinholes. Using such method, we have greatly improved both the PLQY and uniformity of current distribution. As a result, the brightness and the EQE of the PeLEDs have reached



As we can see from Fig. 2a, there are a majority of pin-holes on the films. In addition, the relatively low coverage rate of films can cause much current loss on the interface, which is critical for achieving the good performance of photoelectric devices. What's more, the roughness of the film is also important for fabricating a better photoelectric device. Fig. 2 shows the morphology and the surface roughness of the films, and the quality of pure CsPbBr3 film is terrible with poor coverage and many pinholes in Fig 2a. After adding the PEO in the precursor solution, the coverage of the films is improved significantly. Meanwhile the grain size in CsPbBr3-PEO is significantly reduced, which can improve the coverage and reduce the pinholes of the films. Note that the coverage and compactness of the film is the highest when the PEO concentration is 10 mg/ml. As shown in Fig. 2d,



the amount of pinholes gradually increase with the concentration of PEO increasing to 15 mg/ml. The results may be attributed to the excessive PEO concentration, which limits the spreading of the films during the process of spin-coating.

To further clarify the relationship between concentration and device efficiency, the roughness of the film was studied. **Figure 2**e shows that the root mean square (r.m.s) of the pure CsPbBr<sub>3</sub> films is 34.8 nm. When the PEO concentration is 5 mg/ml, 10 mg/ml, 15 mg/ml, the root mean square is 27.1 nm, 14.7 nm, 96.9 nm respectively, which demonstrate that the surface roughness can be reduced by a specific amount of PEO. From **Fig. 2**f and **Fig. 2**g, we can also note that the grain size reduced significantly, the result is consistent with the previous conclusions.

Figure 3a shows the photoluminescence (PL) spectra of the pure CsPbBr<sub>3</sub> and CsPbBr<sub>3</sub>-PEO films. The

wavelength of the fluorescence peak keeps relatively constant between the CsPbBr3 and PEO assistant CsPbBr3 films, both emission peaks locate at around 521 nm. However, the PL intensity of the CsPbBr3-PEO films under UV illumination 365 nm is more intenser than that of the pure CsPbBr<sub>3</sub> films. Besides, the PLQY 43% which is about six times that of the pure CsPbBr<sub>3</sub> films. As is shown in the photograph (inset of Fig. 3a), the brightness of CsPbBr3-PEO film is much brighter than that of pure CsPbBr3 films which demonstrates that CsPbBr<sub>3</sub>-PEO films can suppress non-radiative decay, which results in a longer PL lifetime as shown in Fig. 3b. Such improvement is likely due to the surface passivation, which is similar to the effects reported in nanocrystals<sup>[13-14]</sup>.The ligand-stabilized luminescent improved morphology of the CsPbBr<sub>3</sub> films leads to excellent electrical properties compared with pure CsPbBr3 films.



Fig 3. (a) PL spectrum (b) PL decay curves of the CsPbBr3 and CsPbBr3-PEO films.

#### 3.2 PeLEDs performance

As shown in Fig 4, the performance of CsPbBr<sub>3</sub>-PEO films is improved in brightness and EQE. The enhanced device performance can be attributed to the improvement in both PLQY and compactness of the films. The relationship between film quality and device performance can also be observed among the perovskite films mixed with different concentration of PEO. The maximum luminance 1432 cd/m<sup>2</sup> has been achieved when the PEO concentration is 10 mg/ml, which is about 10 times of CsPbBr<sub>3</sub> films. The result is due to the reduced pinholes

and compact films, which effectively suppresses the current leakage. The maximum EQE of the PEO based devices are 0.26%, which is about 5 time that of CsPbBr<sub>3</sub> films. The current density and current efficiency also shows the consistent results. From these results we can draw the conclusion that CsPbBr<sub>3</sub>-PEO films possess the better performance. Besides, the concentration of PEO is also important, and 10 mg/ml is the most suitable concentration.



Fig 4. Comparison of PeLEDs performance of CsPbBr<sub>3</sub> and CsPbBr<sub>3</sub>-PEO with different concentrations (a) CD-V characteristic curves of PeLEDs, (b)L-V characteristic curves of PeLEDs, (c)CE-V characteristic curves of PeLEDs, (d) EL characteristic curves of PeLEDs.

# **4 CONCLUSIONS**

In summary, the luminance and the coverage of the perovskite films are successfully improved by adding PEO into the CsPbBr<sub>3</sub> perovskite precursor solution. The amount of PEO is also important to obtain full coverage and pin-hole free emission films. With further optimizing the concentration of PEO, the Current efficiency and external quantum efficiency have reached 0.64 cd/A and 0.26%, respectively. Meanwhile the roughness of the films is decreased significantly. Therefore, this work gives some useful suggestions to improve the coverage, reduce the roughness of the films, and develop high-performance PeLEDs devices, which have a great potential application in a new generation dispalys.

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