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## 30-Fold efficiency enhancement achieved in the perovskite light-emitting diodes†

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Efficient cesium lead halide perovskite light-emitting diodes (PeLEDs) are demonstrated using nearly 100% coverage of CsPbBr<sub>3</sub> film as the emitter. The PeLEDs with only a pumping away process deposited from equimolar PbBr<sub>2</sub>-CsBr exhibit more than 30 fold electroluminescent (EL) performance improvement compared to the ones with both pumping away and annealing processes. And to further improve the EL performance, the molar ratio of PbBr<sub>2</sub> to CsBr is optimized. CsBr-rich PeLEDs (PbBr<sub>2</sub> : CsBr = 1 : 1.2) show longer stability and better EL performance with maximum luminance of 5046 cd m<sup>-2</sup>, maximum current efficiency of 3.25 cd A<sup>-1</sup>, maximum external quantum efficiency (EQE) of 0.85%. The physical mechanism to the enhanced EL performance in the PeLEDs with only pumping away can be attributed to three factors: better coverage rate and smoother surface which reduce current leakage, smaller grain size which can spatially limit the diffusion length of excitons or charge carriers and decrease the possibility of exciton dissociation into carriers, and increased CsBr content of the perovskite precursor solution which may reduce the nonradiative defect densities.

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## 1 Introduction

Since the first room-temperature halide perovskite light-emitting diode (PeLEDs) was demonstrated by Friend's group in 2014,<sup>1</sup> perovskite materials have been considered as promising light emitters and have been paid enormous attraction by worldwide research groups.<sup>2-9</sup> According to their pioneer investigation, it was proved that all-inorganic cesium lead halide perovskite emitters of a common composition CsPbX<sub>3</sub> (X = Cl, Br, and I or mixed halide) have a better thermal stability (up to their melting temperature of about 500 °C) than the organometal ones.<sup>2</sup> And it should be noted that CsPbBr<sub>3</sub> is thermally stable up to 250 °C in air formed *via* solution process.<sup>3</sup> Moreover, it is found that the CsPbBr<sub>3</sub> can provide a high charge-carrier mobility (~1000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>),<sup>5</sup> and low trap density,<sup>6</sup> high photoluminescence (PL) quantum yield (up to 90% in solution),<sup>7,8</sup> and spectra with very high color purity (full width at half maximum, FWHM, ~20 nm) stimulated at room temperature.<sup>9</sup> These attractive thermal and optoelectronic properties of CsPbBr<sub>3</sub> are beneficial to PeLEDs.

One of key factors to achieve high electroluminescent (EL) performance in all-inorganic PeLEDs is to obtain high quality flat and uniform perovskite films with high coverage, and small grains.<sup>10-21</sup> There are two main ways to fabricate all-inorganic

cesium lead halide perovskite films.<sup>11-23</sup> The first way is to prepare perovskite quantum dot films from dispersion of pre-synthesized perovskite colloidal nanocrystals.<sup>12-18</sup> The Kovalenko's method is involved to form the pre-synthesized perovskite colloidal nanocrystals, which needs the protection of N<sub>2</sub> and a high reaction temperature ranged from 100 °C to 200 °C.<sup>24,25</sup> The other way is to obtain perovskite films directly from a perovskite precursor solution.<sup>19-22</sup> The perovskite precursor solution is gained by dissolving both CsBr and PbBr<sub>2</sub> in organic solvent such as dimethyl sulphoxide (DMSO), which is more simple than the Kovalenko's method. Moreover, the film deposited *via* the first way is relatively poor in film coverage due to the insolubility of the perovskite nanoparticle in toluene, and relatively poor conductivity caused by commonly used insulated long-chain surface ligands (such as oleic acid and oleylamine).<sup>14</sup> Thus, the second way is used in this work.

Although the post-treatment processes to the all-inorganic perovskite films deposited *via* the above two methods are different, in most cases, researchers are used to annealing the perovskite films in order to make the films crystallize and the organic solvent volatilize faster to obtain high quality perovskite films with good coverage.<sup>13,16,19,20</sup> To date, for the annealed films formed *via* the first way, the best reported neat CsPbBr<sub>3</sub> quantum dots (QDs) PeLEDs are fabricated from films annealed at 90 °C for 5 min in glove box,<sup>13</sup> showing a maximum luminance of 1698 cd m<sup>-2</sup> for equimolar PbBr<sub>2</sub>-CsBr ones, and 3853 cd m<sup>-2</sup> for CsBr-rich ones (PbBr<sub>2</sub> : CsBr = 1 : 2). While for the films without annealing formed *via* the first way, the best reported one is just dried in air for 10 min<sup>2</sup>, exhibiting maximum

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luminance of  $2335 \text{ cd m}^{-2}$  for the equimolar  $\text{PbBr}_2\text{-CsBr}$  ones. However, for the annealed film *via* the second way, the best reported neat equimolar (CsBr-rich)  $\text{CsPbBr}_3$  PeLEDs are fabricated from films annealed at  $70^\circ\text{C}$  for 5 min ( $70^\circ\text{C}$  for 10 min) in glove box,<sup>20,21</sup> showing a maximum luminance of  $666 \text{ cd m}^{-2}$  ( $4800 \text{ cd m}^{-2}$ ). To improve the luminance, Wei *et al.*<sup>22</sup> developed the third way by firstly obtaining  $\text{CsPbBr}_3$  powder *via* adding CsBr aqueous solution dropwise to the  $\text{PbBr}_2\text{-HBr}$  solution, and secondly dissolving the as-prepared  $\text{CsPbBr}_3$  powder in DMSO, and finally depositing by one-step spin-coating, and obtaining a highest maximum luminance of  $7276 \text{ cd m}^{-2}$  for CsBr-rich ones ( $\text{PbBr}_2 : \text{CsBr} = 1 : 1.4$ ). However, the post-treatment process of the  $\text{CsPbBr}_3$  film is not mentioned in their report and the preparation of the perovskite precursor solution is complicated.

In this paper, we found that the method of pumping away the solvent may be a better choice to make the solvent volatilize quickly and get high quality neat all-inorganic cesium lead halide perovskite  $\text{CsPbBr}_3$  films than the method employing annealing process after pumping away process. The PeLEDs with neat  $\text{CsPbBr}_3$  film gained by only pumping away method after one-step spin-coating, achieve maximum luminances of  $3285 \text{ cd m}^{-2}$  and  $5046 \text{ cd m}^{-2}$ , maximum current efficiencies of  $1.13 \text{ cd A}^{-1}$  and  $3.25 \text{ cd A}^{-1}$ , maximum external quantum efficiency (EQE) of 0.29% and 0.85% from the equimolar  $\text{PbBr}_2\text{-CsBr}$  and CsBr-rich ( $\text{PbBr}_2 : \text{CsBr} = 1 : 1.2$ ) precursor solutions, respectively, which is among the best results based on neat  $\text{CsPbBr}_3$  PeLEDs reported so far. Our results offer a facile method to achieve highly efficient PeLEDs by just pumping away after one-step spin-coating at room temperature.

## 2 Experimental methods

### 2.1 Material and perovskite $\text{CsPbBr}_3$ precursor

Poly(3,4-ethylenedioxythiophene):poly(*p*-styrene sulfonate) (PEDOT:PSS, Clevis AI 4083) was bought from Heraeus (Germany). The 2,2',2''-(1,3,5-benzotriyl)-tris(1-phenyl-1-*H*-benzimidazole) (TPBi), 8-hydroxyquinolino lithium (LiQ), and aluminum (Al) were bought from Suzhou Fangsheng Photoelectricity Shares Co, Ltd and their purity are larger than 99%. The perovskite  $\text{CsPbBr}_3$  precursor solution is obtained by dissolving both  $\text{PbBr}_2$  and CsBr (Xi'an Polymer Light Technology Corp., >99.99%) with molar ratios of 1 : 1 in DMSO (Alfa-Aesar, >99.99%) solvent with a concentration of 10 wt% under constant stirring larger than 12 hours.

### 2.2 Device fabrication

The pre-treated ITO-coated glass substrates, with a sheet resistance of  $\sim 15 \Omega \text{ sq}^{-1}$ , were sequentially pre-cleaned by acetone, ethanol, and deionized water and dried by oven. After ultraviolet ozone treatment for 5 min, PEDOT:PSS was spin-coated on the ITO surface at 4500 rpm for 40 s and then annealed at  $120^\circ\text{C}$  for 20 min. Then, the substrates were transferred into a nitrogen-filled glove box. Next, the  $\text{CsPbBr}_3$  film was formed on the PEDOT:PSS by one-step spin-coating from  $\text{CsPbBr}_3$  precursor solution at 4000 rpm for 60 s with different post-treatment

processes. And then, TPBi (65 nm), Liq (2.5 nm), and Al (120 nm) cathode were evaporated on top of  $\text{CsPbBr}_3$  perovskite film by utilizing a LN-1103SC vacuum thermal depositing system from Shenyang Vacuum Technology Research Institute, where TPBi, Liq/Al are used as an electron transport layer and a bilayer cathode, respectively. The active area of each device was  $2 \times 3 \text{ mm}^2$  which is defined through a shadow mask. All devices were sealed with glass covers in glove box under the protection of  $\text{N}_2$ .

### 2.3 Measurements and characterization

The top-view and cross-section images were taken with a scanning electron microscopy (SEM) system (JEOL, JSM-7100F). The absorption, PL spectra and time-resolved PL spectra were obtained by UV-Vis spectrophotometer (Shimadzu UV-2600) and fluorescence spectrometer (Folurolog 3), respectively. The atomic force microscope (AFM) images and XRD pattern were obtained by Cypher AFM (Cypher S) and X-ray diffractometer (XRD, TD-3500), respectively. The EL performance and stability of PeLEDs were recorded with a LED testing system including Keithley 2400, calculated Si photodiode (Photoelectric Instrument Factory of Beijing Normal University, ST-86LA), and Photo Research SpectraScan photometer (PR 670).

## 3 Results and discussion

### 3.1 Film preparation and surface morphology

The modified and reference neat  $\text{CsPbBr}_3$  films are obtained by one-step spin-coating from 10 wt%  $\text{CsPbBr}_3$  in DMSO solution (shown in Fig. 1a and b). The modified  $\text{CsPbBr}_3$  film is acquired without annealing but only pumping away (Fig. 1c), while the reference  $\text{CsPbBr}_3$  film is annealed at  $70^\circ\text{C}$  for 5 min after pumping away (the top-view SEM images for the optimization of annealing condition can be found in ESI Fig. S1†). And the pumping away is a method to get  $\text{CsPbBr}_3$  perovskite film by pumping the solvent component of the precursor film in the transfer chamber of the glove box for 20 min at room temperature after the spin-coating process as shown in Fig. 1c. The pumping away system is comprised of a transfer chamber belonging to a glove box and attached by a mechanical pump. When the mechanical pump is open, the solvent of the precursor film will be pumped away. From the top view SEM images of the neat  $\text{CsPbBr}_3$  films, it can be found that the coverage of the modified film (Fig. 1d) is improved to 91.1% compared to the reference film (Fig. 1e) of 76.3% (estimated from SEM images by using ImageJ software), and the average grain size is reduced to  $\sim 100 \text{ nm}$  compared to that of the reference film of  $\sim 110 \text{ nm}$ . Higher coverage and smaller grains suggest that better EL performance can be achieved in the modified film based PeLEDs. In Fig. 1f, similar absorption spectra shapes are demonstrated in both modified and reference neat  $\text{CsPbBr}_3$  films with absorption band edges of 539 nm and 542 nm, respectively. From the PL spectra in Fig. 1f, it suggests that the both modified and reference neat  $\text{CsPbBr}_3$  films have the same emission peaks (520 nm) and same FWHM ( $\sim 18 \text{ nm}$ ). However, the modified neat  $\text{CsPbBr}_3$  film exhibits



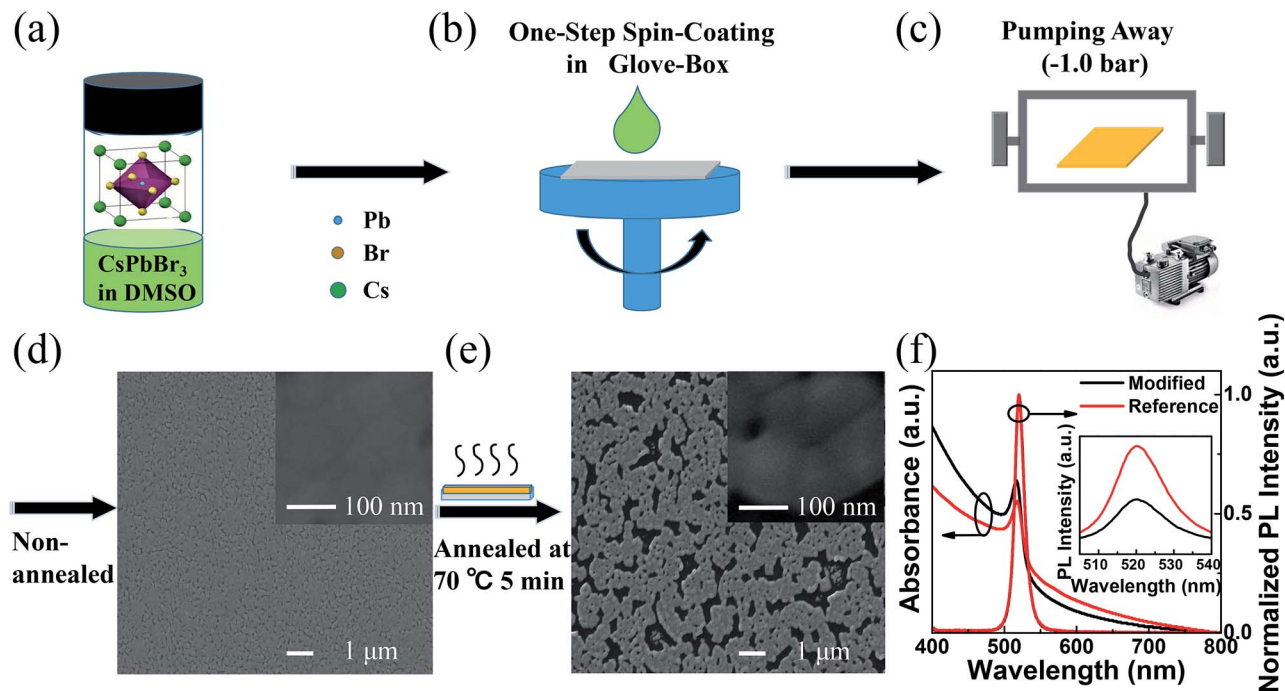


Fig. 1 The schematic diagram of (a) preparation of 10 wt% CsPbBr<sub>3</sub> in DMSO precursor solution, (b) one-step spin-coating method, (c) pumping away method, (d) the top-view SEM image of modified neat CsPbBr<sub>3</sub> film without annealing only pumping away, (e) the top-view SEM image of reference neat CsPbBr<sub>3</sub> film which is annealed at 70 °C for 5 min after pumping away, (f) the absorption and normalized PL spectra of modified and reference neat CsPbBr<sub>3</sub> film. The inset exhibits the PL intensity of modified and reference neat CsPbBr<sub>3</sub> films excited with equal light intensity at 365 nm.

remarkably higher PL intensity compared to the reference neat CsPbBr<sub>3</sub> film excited with equal light intensity at 365 nm (shown in the inset of Fig. 1f). Since the EL efficiency of PeLEDs is proportional to the PL intensity of perovskite, the improvement of PL properties in modified neat CsPbBr<sub>3</sub> thin films with only pumping away will be expected to improve the EL efficiency in the modified neat CsPbBr<sub>3</sub> thin films based PeLEDs.<sup>19</sup>

### 3.2 PeLEDs performance

Using the modified neat CsPbBr<sub>3</sub> film as the light emitter, the PeLEDs exhibit improved EL performance. The PeLEDs employ a typical layered structure of ITO/PEDOT:PSS<sub>30 nm</sub>/(reference or modified) neat CsPbBr<sub>3</sub> film/TPBi<sub>65 nm</sub>/Liq<sub>2.5 nm</sub>/Al. According to the cross-section SEM image of the PeLEDs (Fig. 2a), the thickness of the modified neat CsPbBr<sub>3</sub> film is estimated to ~30 nm. The schematic diagram of the PeLEDs structure is shown section SEM image of the neat CsPbBr<sub>3</sub> film based PeLEDs. The energy level diagram of each layer is shown in Fig. 2c, and all energy level values were taken from literature.<sup>26–28</sup> The current density–voltage–luminance (*J*–*V*–*L*) relationship and the current efficiency–voltage–EQE (CE–*V*–EQE) relationship are shown in Fig. 2d and e, respectively. From *J*–*V* relationship, the modified neat CsPbBr<sub>3</sub> film based PeLEDs exhibit lower density than reference film based ones at each applied voltage. It suggests that less current leakage in the modified PeLEDs than that in the reference ones due to higher film coverage and less pinholes in the modified film which is consistent to the top-view SEM results. From the *L*–*V*

relationship and CE–*V*–EQE relationship, the modified neat CsPbBr<sub>3</sub> film based PeLEDs exhibit higher luminance, current efficiency and EQE than the reference film based ones at each applied voltage, and showing maximum luminance of 3285 cd m<sup>-2</sup>, maximum current efficiency of 1.13 cd A<sup>-1</sup> and maximum EQE of 0.29%, which are 30 times more than that of the PeLEDs with annealing process (70 °C/5 min) showing maximum luminance of 103 cd m<sup>-2</sup>, maximum current efficiency of 0.017 cd A<sup>-1</sup> and maximum EQE of 0.004%. The enhance EL performance can be attributed to both higher film coverage which can make the current leakage decreased<sup>16,26</sup> and smaller grain size which can spatially limit the diffusion length of excitons or charge carriers and decrease the possibility of exciton dissociation into carriers. Fig. 2f shows the EL spectra of modified neat CsPbBr<sub>3</sub> film based PeLEDs at different applied voltage, which exhibit a high color purity of FWHM ~18 nm and a peak wavelength located at 522 nm. In the inset of Fig. 2f, the EL color is stable and the shapes of the EL spectra are independent with applied voltage, which suggest that CsPbBr<sub>3</sub> PeLEDs can be potentially adopted as good light sources.

### 3.3 Optimizations of PeLEDs

The improved EL performance of modified film based PeLEDs can be attributed to the higher film coverage and smaller grain size, which are related to the facile and efficient film post-treatment process of only pumping away method. To further investigate the physical mechanism for the enhanced EL performance in CsPbBr<sub>3</sub> PeLEDs with only pumping away, both





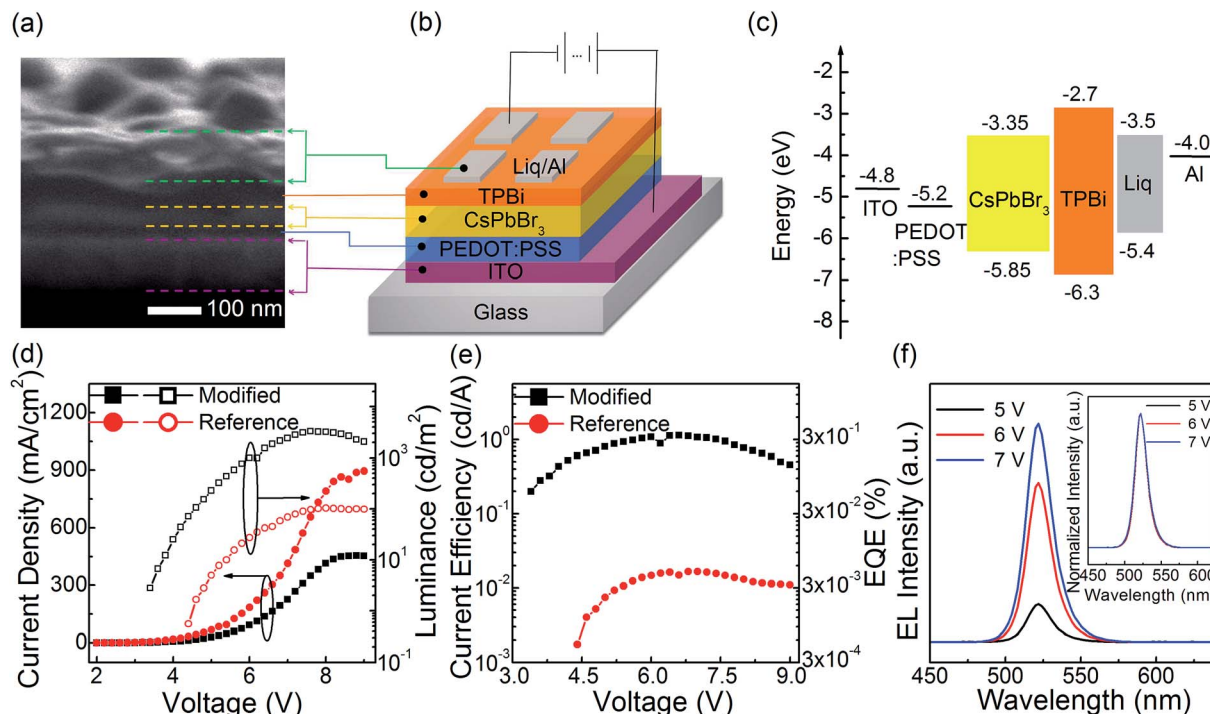


Fig. 2 (a) The cross-section SEM image of the PeLEDs with modified neat CsPbBr<sub>3</sub> film, (b) the schematic diagram of the PeLEDs structure, (c) energy level diagram of PeLEDs, (d)  $J$ - $V$ - $L$  characteristics of the PeLEDs, (e) CE- $V$ -EQE relationship of the PeLEDs, (f) EL spectra of the PeLEDs based on modified neat CsPbBr<sub>3</sub> film applied at different voltages of 5 V, 6 V, and 7 V. The inset shows the normalized EL spectra of the modified neat CsPbBr<sub>3</sub> film based PeLEDs working at 5 V, 6 V, and 7 V.

the optimization of the CsPbBr<sub>3</sub> concentration in DMSO precursor solution and the optimization of the molar ratio of PbBr<sub>2</sub> to CsBr will be discussed.

**3.3.1 Optimization for the CsPbBr<sub>3</sub> concentration.** Fig. 3a, b and c show the top-view SEM images of modified neat CsPbBr<sub>3</sub> films (with only pumping away) deposited from concentrations of 5 wt%, 10 wt%, and 15 wt% in DMSO precursor solution, respectively. For all the films with different concentrations, CsPbBr<sub>3</sub> grains are irregular, which are just as same as the published results in ref. 19. It can be found that both the film coverage rate and the size of the grains rise with the increase of CsPbBr<sub>3</sub> concentration in DMSO. The coverage rates and grain sizes are estimated to ~49.1% and ~90 nm, ~91.1% and ~100 nm, ~96.9% and ~130 nm for the films with concentrations of 5 wt%, 10 wt% and 15 wt%, respectively. From the  $J$ - $V$  relationship (Fig. 3d),  $L$ - $V$  relationship (Fig. 3e) and CE- $V$ -EQE relationship (Fig. 3f), it can be found that the current density decreases with the increase of CsPbBr<sub>3</sub> concentration at each applied voltage, while the PeLEDs based on the 10 wt% CsPbBr<sub>3</sub> film reveals the best EL performance with maximum luminance of 3285 cd m<sup>-2</sup>, maximum current efficiency of 1.13 cd A<sup>-1</sup>, and maximum EQE of 0.29% (Fig. 3e). Two factors should be taken into consideration for the best EL performance in modified 10 wt% CsPbBr<sub>3</sub> film based PeLEDs film coverage and grain size. The coverage rates of modified CsPbBr<sub>3</sub> film with concentrations of 10 wt% are higher than that of modified CsPbBr<sub>3</sub> film with concentrations of 5 wt%, but lower than that of modified CsPbBr<sub>3</sub> film with concentrations of 15 wt%. And

grain sizes of modified CsPbBr<sub>3</sub> films with concentrations of 10 wt% are larger than that of modified CsPbBr<sub>3</sub> film with concentrations of 5 wt%, but smaller than that of modified CsPbBr<sub>3</sub> film with concentrations of 15 wt%. The lower coverage rate makes the current leakage increase, which is bad to the EL performance of PeLEDs, while the smaller grains make the excitons undergo radiative recombination, which is beneficial to the EL performance of PeLEDs. These two aspects compete mutually and the current efficiency (CE) is defined as:  $CE = L/J$ , where the  $L$  and  $J$  represent the luminance and current density at each applied voltage of the PeLEDs, respectively. As a result, the PeLEDs using 10 wt% CsPbBr<sub>3</sub> film exhibit the best EL performance with suitable coverage rate and grain size. Meanwhile, for the PeLEDs using 5 wt% CsPbBr<sub>3</sub> film show a greater current density at each applied voltage and an inferior EL performance compared to PeLEDs based on 10 wt% CsPbBr<sub>3</sub> film, which suggests that the lower coverage rate plays a leading role in weakening the EL performance in 5 wt% CsPbBr<sub>3</sub> film based PeLEDs. When it comes to the PeLEDs using 15 wt% CsPbBr<sub>3</sub> film, it exhibits a lower current density at each applied voltage and an inferior EL performance compared to PeLEDs based on 10 wt% CsPbBr<sub>3</sub> film, which suggests that larger grain size plays a leading role to reduce the current efficiency in the PeLEDs with 15 wt% CsPbBr<sub>3</sub> film.

**3.3.2 Optimization for the molar ratio of PbBr<sub>2</sub> to CsBr.** Besides optimization for the CsPbBr<sub>3</sub> concentration in DMSO precursor solution, the PeLEDs with different molar ratios of PbBr<sub>2</sub> to CsBr equaling to 1.1 : 1, 1 : 1, 1 : 1.2, and 1 : 1.4 at



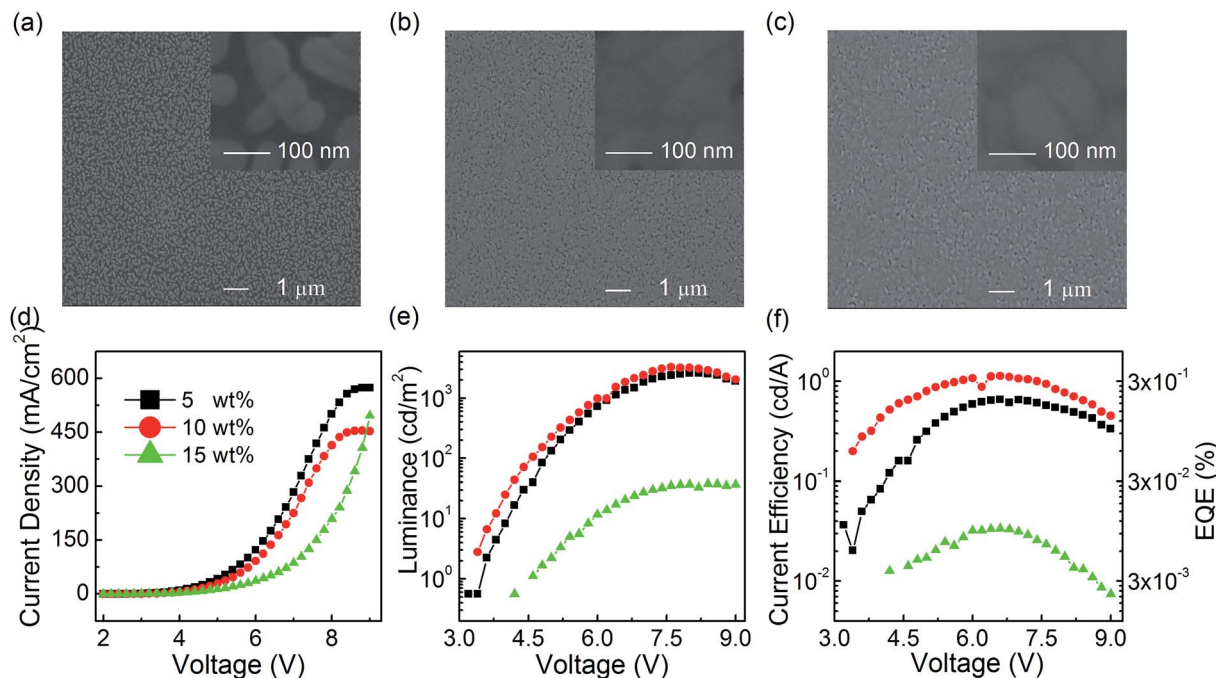


Fig. 3 The top-view SEM image of modified neat CsPbBr<sub>3</sub> film with only pumping away from different concentrations of (a) 5 wt%, (b) 10 wt%, (c) 15 wt% in DMSO precursor solution, (d)  $J$ - $V$ - $L$  relationship, (e)  $L$ - $V$  of the PeLEDs, (f) CE- $V$ -EQE relationship of the PeLEDs based on different CsPbBr<sub>3</sub> concentrations in DMSO precursor solution.

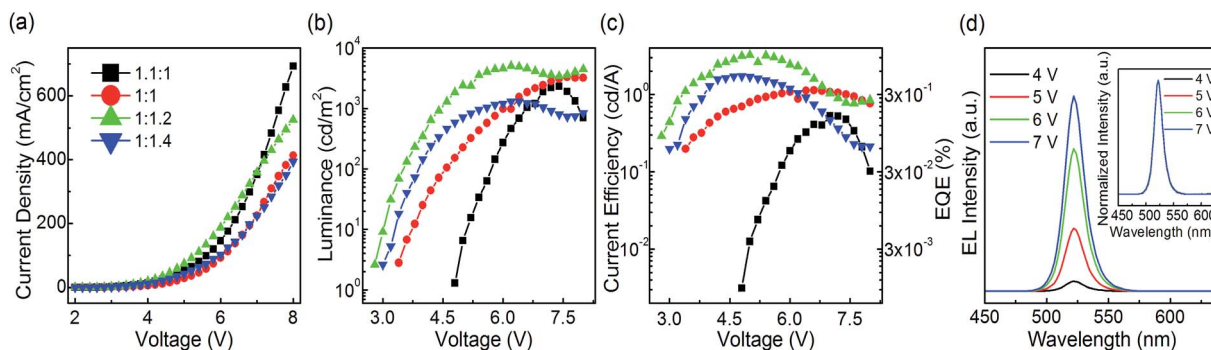


Fig. 4 (a)  $J$ - $V$  relationship, (b)  $L$ - $V$  relationship, (c) CE- $V$ -EQE relationship of the PeLEDs with only pumping away and different molar ratios of PbBr<sub>2</sub> to CsBr of 1:1, 1:1, 1:1.2, and 1:1.4 at a 10 wt% CsPbBr<sub>3</sub> concentration in DMSO precursor solution, (d) EL spectra of the PeLEDs based on modified neat CsPbBr<sub>3</sub> film molar ratio of PbBr<sub>2</sub> to CsBr of 1:1.2 at a 10 wt% CsPbBr<sub>3</sub> concentration in DMSO precursor solution with applied at different voltages of 4 V, 5 V, 6 V, and 7 V. The inset shows the normalized EL spectra of the modified neat 10 wt% CsPbBr<sub>3</sub> PeLEDs based on the molar ratio of PbBr<sub>2</sub> to CsBr equaling to 1:1.2 working at 4 V, 5 V, 6 V, and 7 V.

a 10 wt% CsPbBr<sub>3</sub> concentration in DMSO precursor solution are fabricated with only pumping away process. From the  $J$ - $V$  curves, the PeLEDs based on the molar ratio of PbBr<sub>2</sub> to CsBr equaling to 1:1.2 exhibit the largest current density among all PeLEDs at each applied voltage lower than 7 V. When it comes to the  $L$ - $V$  relationship, the PeLEDs with a molar ratio of PbBr<sub>2</sub> to CsBr of 1:1.2 exhibit the highest maximum luminance of 5046 cd m<sup>-2</sup> and lowest turn on voltage of 2.8 V among all the devices. Moreover, the current efficiency and EQE of the PeLEDs with a molar ratio of PbBr<sub>2</sub> to CsBr equaling to 1:1.2 show the best with maximum current efficiency of 3.25 cd A<sup>-1</sup> and maximum EQE of 0.85% among all the devices, which is among

the best results based on neat CsPbBr<sub>3</sub> PeLEDs reported so far. It should be noted that the maximum current efficiency and the maximum EQE of PeLEDs increase with the CsBr proportion increasing in all the PeLEDs. This enhancement in EL performance is attributed to the Br-rich passivation that can reduce the halogen vacancies ( $V_{\text{Br}}$ ) (e.g. decreasing the non-radiative recombination), and thus leading to improved EL performance. This is verified by previous theoretical<sup>29</sup> studying. Previous theoretical density functional theory (DFT) demonstrate that the presence of  $V_{\text{Br}}$  on CsPbBr<sub>3</sub> plays a role as defects within the band gap and acts as recombination centers. The deposition from CsBr-rich solution may reduce the probability



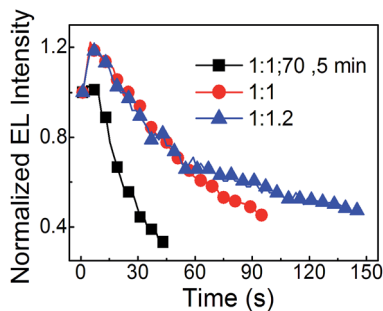


Fig. 5 The stability of PeLEDs formed by  $\text{PbBr}_2 : \text{CsBr} = 1 : 1$  with annealing at  $70^\circ\text{C}$  for 5 min after pumping away,  $\text{PbBr}_2 : \text{CsBr} = 1 : 1$  with just pumping away, and  $\text{PbBr}_2 : \text{CsBr} = 1 : 1.2$  with just pumping away.

of  $V_{\text{Br}}$  formation on the films and hence reduce the non-radiative defect densities. And this is demonstrated by previous experimental<sup>19</sup> and the time-resolved PL measurements we conducted. The time-resolved PL spectra are exhibited in the Fig. S2.† The average radiative recombination lifetime of the  $1 : 1.2$  neat  $\text{CsPbBr}_3$  films (0.86 ns) with only pumping away is larger than  $1 : 1$  neat  $\text{CsPbBr}_3$  films (0.82 ns). The result suggests that Br additive can effectively passivate the grain boundaries, and thus reducing non-radiation recombination, leading to enhanced the EL performance in the  $1 : 1.2$  neat  $\text{CsPbBr}_3$  films based PeLEDs. And the PeLEDs with molar ratio of  $1 : 1.2$  also show stable color with a high color purity of FWHM  $\sim 18$  nm and a peak wavelength located at 522 nm at different applied voltages (show in Fig. 4d and its inset).

**3.3.3 The stability of PeLEDs.** As shown in Fig. 5, the stability of both equal molar ratio of  $\text{PbBr}_2 : \text{CsBr}$  and CsBr rich ( $\text{PbBr}_2 : \text{CsBr} = 1 : 1.2$ ) neat  $\text{CsPbBr}_3$  PeLEDs with just pumping away are better than that of neat  $\text{CsPbBr}_3$  PeLEDs with annealing. The half lifetimes (which is the time duration from the initial luminance of  $100 \text{ cd m}^{-2}$  decreasing to half luminance of the initial luminance) of the three PeLEDs formed by  $\text{PbBr}_2 : \text{CsBr} = 1 : 1$  with annealing at  $70^\circ\text{C}$  for 5 min after pumping away,  $\text{PbBr}_2 : \text{CsBr} = 1 : 1$  with just pumping away, and  $\text{PbBr}_2 : \text{CsBr} = 1 : 1.2$  with just pumping away are estimated to 29 s, 87 s and 135 s, respectively. It indicates that the

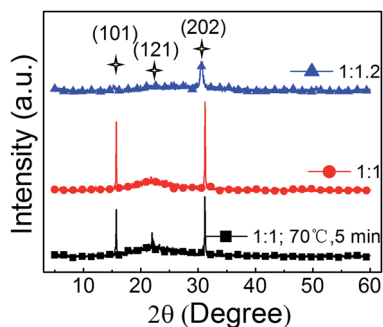


Fig. 6 The XRD patterns of three 10 wt% neat  $\text{CsPbBr}_3$  films ( $\text{PbBr}_2 : \text{CsBr} = 1 : 1$  with annealing at  $70^\circ\text{C}$  for 5 min after pumping away,  $\text{PbBr}_2 : \text{CsBr} = 1 : 1$  with just pumping away,  $\text{PbBr}_2 : \text{CsBr} = 1 : 1.2$  with just pumping away).

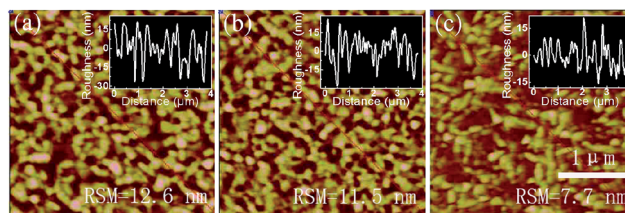


Fig. 7 AFM images for three 10 wt% neat  $\text{CsPbBr}_3$  films (a)  $\text{PbBr}_2 : \text{CsBr} = 1 : 1$  with annealing at  $70^\circ\text{C}$  for 5 min after pumping away, (b)  $\text{PbBr}_2 : \text{CsBr} = 1 : 1$  with just pumping away, (c)  $\text{PbBr}_2 : \text{CsBr} = 1 : 1.2$  with just pumping away.

pumping away process and the Br rich method are benefit to make the PeLEDs more stable.

### 3.4 XRD patterns of perovskite films

In Fig. 6, the XRD patterns of the three neat  $\text{CsPbBr}_3$  films ( $\text{PbBr}_2 : \text{CsBr} = 1 : 1$  with annealing at  $70^\circ\text{C}$  for 5 min after pumping away,  $\text{PbBr}_2 : \text{CsBr} = 1 : 1$  with just pumping away,  $\text{PbBr}_2 : \text{CsBr} = 1 : 1.2$  with just pumping away) indicate that orthorhombic crystal structures are realized. And no additional peak for the solvent residue are found in the XRD patterns, which means that there is no solvent residue in all the three films. To further confirm it, the UV-Vis absorption spectra are shown in Fig. S3,† and similar absorption shapes are demonstrated. These results suggest that the structures and the optical properties of perovskite films with just pumping away are same with that of the one with annealing, which may not do bad effects to the EL performance.

### 3.5 AFM images of perovskite films

AFM images are performed and are shown in Fig. 7. For the neat  $1 : 1$   $\text{CsPbBr}_3$  films, the annealed one exhibits a larger roughness of 12.6 nm compared to the one without annealing (11.5 nm), which indicating that annealing after the pumping away process will do bad effect to the morphology of the perovskite film and leading to worse EL performance of the PeLED with annealed neat  $1 : 1$   $\text{CsPbBr}_3$  film. And with only pumping away process, the surface roughness can be further reduced to 7.7 nm by Br rich  $\text{CsPbBr}_3$  film with  $\text{PbBr}_2 : \text{CsBr}$  equaling to  $1 : 1.2$ . Thus, with the smoothest  $\text{CsPbBr}_3$  film, the PeLEDs with molar ratio of  $1 : 1.2$  achieved the best EL performance.

## 4 Conclusion

The simple and effective method of only pumping away process is demonstrated to fabricate equimolar and CsBr-rich  $\text{CsPbBr}_3$  PeLEDs with enhanced EL performance of maximum luminance of  $3285 \text{ cd m}^{-2}$  and  $5046 \text{ cd m}^{-2}$ , maximum current efficiency of  $1.13 \text{ cd A}^{-1}$  and  $3.25 \text{ cd A}^{-1}$  and EQE of 0.29% and 0.85%, which are 30 folds more than that of the equimolar ones with  $70^\circ\text{C}/5$  min annealing process after pumping away process. The only pumping away process benefits to obtain high quality  $\text{CsPbBr}_3$  film with higher coverage, smaller grains better Br-rich passivation, and smoother surface, which lead to less





current leakage, and larger possibility of exciton radiative decay, and thus achieving better EL performance and longer stability in PeLEDs with only pumping away. The work therefore offers some helpful implications in developing high-performance PeLEDs.

## Conflicts of interest

There are no conflicts of interest to declare.

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