PHYSICAL CHEMISTRY

Efficient Inorganic Perovskite Light-Emitting Diodes with Polyethylene Glycol Passivated Ultrathin CsPbBr₃ Films

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Supporting Information

ABSTRACT: Efficient inorganic perovskite light-emitting diodes (PeLEDs) with an ultrathin perovskite emission layer (~30 nm) were realized by doping Lewis base polyethylene glycol (PEG) into CsPbBr₃ films. PEG in the perovskite films not only physically fills the crystal boundaries but also interacts with the perovskite crystals to passivate the crystal grains, reduce nonradiative recombination, and ensure efficient luminance and high efficiency. As a result, promoted brightness, current efficiency (CE), and external quantum efficiency (EQE) were achieved. The nonradiative decay rate of the PEG:CsPbBr₃ composite film is 1 order of magnitude less than that of the neat CsPbBr₃ film. After further optimization of the molar ratio between CsBr and PbBr₂, a peak CE of 19 cd/A, a maximum EQE of 5.34%, and a maximum brightness of 36600 cd/m² were achieved, demonstrating the interaction between PEG and the precursors. The results are expected to offer some helpful implications in optimizing the



polymer-assisted PeLEDs with ultrathin emission layers, which might have potential application in see-through displays.

B y virtue of the superior optical and electrical characteristics of the metal-halide perovskite semiconductors including high absorption coefficients, long diffusion length, and high mobility,^{1,2} the power conversion efficiencies of the perovskite solar cells have reached in excess of 20% in just a few years.³⁻⁵ Besides the remarkable achievement in photovoltaic devices, perovskites are also promising candidates for next-generation light-emitting devices owing to their high photoluminescence quantum efficiency (PLQY), high color rendering ability, and abundant colors by mixing different halide compounds with varied stoichiometric ratio.⁶⁻⁸

In the past few years, perovskite light-emitting diodes (PeLEDs) based on organic-inorganic lead halides (MAPbX₃ with X= I, Br, Cl; MA = CH_3NH_3) have been widely studied, 9^{-13} and significant advances in both brightness and current efficiency (CE) have been made through device structure,¹⁴ morphology,^{15,16} and precursor stoichiometry control.¹⁷ Recently, a high CE of 42.9 cd/A together with a high external quantum efficiency (EQE) of 8.53% based on a MAPbBr₃ PeLED has been achieved by Cho et al., encouraging research and development of PeLEDs.¹⁸ However, the organic-inorganic hybrid PeLEDs suffer from poor stability under high humidity and during long-term operation, which significantly hinders their application.¹⁹⁻²¹ Additionally, owning to the poor film morphology that resulted from the large grain size in the emissive films, most of the reported organicinorganic hybrid PeLEDs utilized thick emission layers (>50 nm) to increase the film coverage and minimize the current leakage.^{18,22,23} However, the thick emissive films could lead to obvious self-absorption loss and limit device applications in some special domains, especially in see-through displays, such as window displays, automotive windshield displays, head-mounted displays, and so forth.

Thanks to materials development, the stability of organicinorganic hybrid PeLEDs can be significantly promoted by replacing the unstable organic MA cation with an inorganic Cs cation, boosting the development of high-performance PeLEDs with excellent stability.²⁴⁻²⁶ Among the reported inorganic PeLEDs, CsPbBr₃ is the most studied perovskite emitter.^{26–29} Recently, PeLEDs with CsPbBr₃ films fabricated by a facile onestep solution method³⁰⁻³² were proposed and became attractive in terms of more efficient PLQY in the emissive films and higher electroluminescence (EL) performance, enabling a thin perovskite emission layer with less selfabsorption loss to achieve high device performance. Therefore, besides the superior thermal and chemical stability, the CsPbBr₃ film-based PeLEDs could be more favorable to realize efficient transparent devices for potential application in seethrough displays. To realize efficient PeLEDs based on CsPbBr₃ films, high-quality CsPbBr3 perovskite films with small and uniform crystal grains and reduced defect states are the preconditions,^{18,21} which is in favor of spatially confining the injected charges to facilitate exciton formation, increase radiative recombination, and suppress nonradiative recombination. For this purpose, several methods have been carried out to adjust the grain size and modify the morphology engineering of

Received:
 July 6, 2017

 Accepted:
 August 17, 2017

 Published:
 August 17, 2017

the perovskite films. One of the intelligent strategies is blending the perovskite precursors with a polymer dielectric, such as poly(ethylene oxide),³³ polyhedral oligomeric silsesquioxane,³⁴ and poly(2-ethyl-2-oxazoline),²³ originating from organometal hybrid devices, by which the inorganic PeLED performance has been improved dramatically (e.g., brightness from several hundred to tens of thousands cd/m² and CEs from 0.035 to 33.9 cd/A).^{25,31,35–37} However, the physical mechanism of the interaction between perovskites and polymers has not been revealed and discussed profoundly, and the PeLEDs fabricated by a simple one-step method based on ultrathin CsPbBr₃ perovskite films (<50 nm) with outstanding device performance have been rarely reported.

Herein, we successfully realized high-performance CsPbBr₃ PeLEDs by introducing the nonionic dielectric polyethylene glycol (PEG) into perovskite precursors to form ultrathin (~30 nm) PEG:CsPbBr3 composite films. The optimized PEG:CsPbBr₃ PeLED achieved a maximum luminance of 38900 cdm⁻², a peak CE of 4.26 cd/A, and a maximum EQE of 1.2%, much higher than those of the PeLED with a pristine CsPbBr₃ layer. Compared with the neat CsPbBr₃ film, the calculated nonradiative decay rate of the composite film was obviously reduced. Such achievement can be attributed to the decreased crystal grain size, passivated nonradiative defects, and suppressed nonradiative current loss, which are verified to originate from the interaction between PEG and CsPbBr₃. By further cautiously tuning the molar ratio between CsBr and PbBr₂, superior performance including a remarkably improved peak CE of 19 cd/A and maximum EQE of 5.34% was achieved. We expect that the results would provide some implications in developing polymer additive-assisted PeLEDs with high performance. The efficient PeLEDs based on the thin perovskite films will be beneficial to realizing transparent devices for the potential application in see-through displays.

The conventional PeLED structure of ITO/PEDOT:PSS/ perovskite/TPBi/LiF/Al was introduced in this work. The cross section scanning electron microscopy (SEM) image and the corresponding energy level diagram of the typical inorganic PeLED are shown in Figure 1a,b, respectively. It is seen that the thickness of the perovskite layer is about 30 nm in Figure 1a, which is the thinnest perovskite-emitting layer among the reported inorganic PeLEDs. Also, the ultrathin perovskite film is confirmed by the cross-sectional atomic force microscopy (AFM) profile of the scratched films (Figure S1). The EL characteristics of the PeLEDs with a fixed CsBr:PbBr₂ molar ratio of 1.4:1 and different PEG ratios were investigated first. Figure 1c-f displays the current density-voltage (I-V), luminance-voltage (L-V), CE-voltage (CE-V), as well as EQE-voltage (EQE-V) curves for the PeLEDs with different PEG:CsPbBr3 weight ratios of 0:1, 0.023:1, 0.034:1, and 0.042:1, respectively, and the detailed device parameters are summarized in Table 1. The reference device without PEG doping in the CsPbBr₃ emission layer shows a turn-on voltage (V_{on}) of 3.2 V, a maximum luminance of 4800 cd/m² at 6.4 V, a maximum CE of 1.12 cd/A, and an EQE of 0.31%. Although the maximum brightness of the reference device is a bit lower than that of the previous report (7276 cd/m^2) ,²⁶ the maximum CE and EQE of this reference device are approximately two times higher than that of the reported values (0.57 cd/A and 0.15%, respectively), indicating good state-of-the-art in preparing our PeLEDs. As a different amount of PEG was added in the CsPbBr₃ precursor solution, the device performance was improved gradually and achieved an optimized device



Figure 1. (a) Device structure of the PeLED. (b) Schematic diagram of energy levels for different layers of the PeLED. (c) J-V curves, (d) L-V curves, (e) CE-V curves, and (f) EQE-V curves for the PeLEDs with different PEG:CsPbBr₃ (CsBr:PbBr₂ molar ratio of 1.4:1) weight ratios.

Table 1. EL Performance of the PeLEDs with Different PEG:CsPbBr₃ Weight Ratios in Perovskite-Emitting Layers

weight ratio of PEG:CsPbBr ₃	max. luminance (cd/m²)	max. CE (cd/A)	max. EQE (%)	turn-on voltage (V)	voltage @ max. luminance (V)
0:1	4800	1.12	0.31	3.2	6.4
0.023:1	27400	3.19	0.90	2.9	6.6
0.034:1	38900	4.26	1.20	2.8	5.8
0.042:1	24700	3.98	1.12	2.8	6.4

performance with a V_{on} of 2.8 V, a maximum luminance of 38900 cd/m² at 5.8 V, a maximum CE of 4.26 cd/A, and a maximum EQE of 1.2% at the PEG:CsPbBr₃ weight ratio of 0.034:1. A sharp decrease in EQE is seen for the optimal device when the drive voltage is higher than 5 V, which may originate from the higher current density, as shown in Figure S2, where all of the devices show quite identical behavior.

The spectra of the PEG:CsPbBr₃ devices are shown in Figure 2a,b. The EL spectrum curve for the PEG:CsPbBr₃ presents a sharp emission peak centered at around 522 nm with a full width at half-maximum (fwhm) of 16 nm, which is consistent with the PL spectrum located at the edge of the absorption band, suggesting the direct recombination at the band edge (Figure 2a). Meanwhile, there is no peak drift as the voltage varies from 3 to 6 V with a step of 0.3 V, indicating the stable color purity of the PeLEDs with PEG:CsPbBr₃ composite emissive layers (Figure 2b). The narrow and stable EL spectra enable high color rendering ability. The 1931 Commission Internationale de l'Eclairage (CIE) color coordinate is (0.13,



Figure 2. (a) Absorption, PL spectra for the PEG:CsPbBr₃ film and EL spectrum for the PeLED with PEG:CsPbBr₃ as the emission layer. (b) EL spectra for the device as the voltage varies from 3 to 6 V. The inset is a photograph of the PeLED under working conditions.

0.77), indicating a pure green light emission, and a photo of the PeLED under working condition is exhibited in the inset of Figure 2b.

To provide deep insight into the enhancement of the device performance when PEG was introduced into the CsPbBr₃ film, both the SEM and AFM images were performed and are shown in Figure 3 to investigate the effect of PEG on the morphology of the perovskite thin films. The SEM images show a similar tendency in agreement with the AFM results. As shown in Figure 3a,e, the pristine CsPbBr₃ thin films are composed of many large grains and thus a rough surface morphology with a high roughness of 9.593 nm. The poor film morphology leads to large nonradiative current losses through the pinholes, and thus, limiting the charge injection in the controlled PeLED further results in high V_{on} and low brightness and light-emitting efficiency (Table 1). When a small amount of PEG was added in the CsPbBr₃ thin films with a PEG:CsPbBr₃ weight ratio of 0.023:1 (Figure 3b,f), the number of large grains reduced obviously, and small grains appeared in the PEG:CsPbBr₃ composite perovskite films. We believe that the CsPbBr₃ grain size is limited by the additive PEG. Meanwhile, the surface roughness of the composite perovskite film decreased to 6.269 nm. As the PEG:CsPbBr₃ weight ratio further increased to 0.034:1 (Figure 3c,g), the large grains in the PEG:CsPbBr₃ films were further decreased and the composite perovskite films became more uniform. When the PEG:CsPbBr₃ weight ratio finally increased to 0.042:1 (Figure 3d,h), despite the small grains, much more empty space between the grains appeared in the film, resulting in large surface roughness (11.936 nm) and poor film coverage and thus lowered the EL performance of the PeLED. In a word, small and uniform grains in the

PEG:CsPbBr₃ composite perovskite emissive films are of great importance to realize efficient PeLEDs.

Interestingly, compared with the neat CsPbBr₃ film, the composite perovskite film with a PEG:CsPbBr₃ weight ratio of 0.042:1 is seen for more segregated grains (Figure 3), while the corresponding PeLED device still maintains higher brightness and CE than that of the reference device. Although the X-ray diffraction pattern of the PEG:CsPbBr3 film does not exhibit the characteristic peaks of PEG (Figure S3),³⁸ we still speculate that there is a small amount of PEG residual in the composite perovskite film. Actually, the boiling point of PEG is more than 250 °C,³⁹ while the annealing temperature of the composite perovskite film was only 70 °C. Hence, it is reasonable for our assumption that a small amount of PEG remained in the composite perovskite film, which might fill the gaps between perovskite crystals. Thereafter, the long-chain PEG in the evenly mixed CsBr-PbBr₂-PEG precursor solution would act as a polymer scaffold and prevent the perovskite precursors from diffusing during the fabrication process of composite perovskite films, including spin-coating and annealing. As a result, small and uniform perovskite crystals were achieved.

It is worth mentioning that $PbX_2(X = Cl, Br, I)$ is a wellknown Lewis acid that would form an adduct with a Lewis base possessing oxygen, nitrogen, and sulfur electron-donating atoms via weak chemical interaction.⁴⁰ The interaction between the Lewis acid Pb²⁺ and Lewis base can contribute to highquality perovskite films and thus improve the photovoltaic performance in solar cells.^{41–43} What's more, the passivation of the perovskite crystal's surface by a Lewis base can also significantly reduce the nonradiative exciton recombination.^{44,45} Hence, the reduction of the nonradiative recombination probably originated from the interaction between PEG and Pb²⁺. To verify this assumption, Fourier-transform infrared (FTIR) was performed to clearly study how the PEG interacts with the CsPbBr₃. Figure 4a showed the FTIR spectra for powdered PEG, PEG:PbBr₂, and PEG:CsPbBr₃. For the pure PEG, the C-O-C stretching vibration frequency appears at 950 cm^{-1,46} while for the PEG:PbBr₂ compound, as the Lewis base PEG combined with the Lewis acid Pb^{2+} , the C-O-C stretching vibration frequency is red-shifted to 937 cm⁻¹ owing to the reduced force constant of C-O-C, which is related to the stretching vibration frequency in the diatomic harmonic motion model. This frequency is further shifted to 932 cm^{-1} for the PEG:CsPbBr₃ compound, thereby demonstrating the strengthened interaction between the PEG and CsPbBr₃. According to the above results, it can be concluded that the remaining PEG in the perovskite films not only physically fills



Figure 3. SEM and AFM images for the perovskite films with different PEG:CsPbBr₃ weight ratios: (a,e) for 0:1; (b,f) for 0.023:1; (c,g) for 0.034:1; and (d,h) for 0.042:1.



Figure 4. (a) FTIR spectra of PEG, PEG:PbBr₂, and PEG:CsPbBr₃ powders. (b) Normalized PL intensity and PLQY as a function of the PEG:CsPbBr₃ weight ratio. (c) Time-resolved PL decay curves for neat CsPbBr₃ and PEG:CsPbBr₃ (0.034:1) films.

the crystal boundaries but also interacts with the perovskite crystals to passivate the crystal grains, reduce nonradiative recombination, and ensure efficient luminance and high efficiency.

In order to further reveal the effect of PEG, more particular measurements were carried out. Steady-state and time-resolved PL measurements were adopted to investigate the luminescent properties of the perovskite films before and after PEG doping. Figure 4b shows the steady-state PL intensity and PLQY as a function of the amount of PEG additive. The variation tendencies of the PL intensities and PLQYs are consistent with the changes in PeLED brightness (Table 1). The composite perovskite film with a PEG weight ratio of 0.034:1 presents the strongest PL intensity and the maximum PLQY of 35% (Table S1) due to the smaller uniformly distributed perovskite crystals (Figure 3), suggesting the decreased surface defects or traps probably passivated by PEG and the heightened PLQY of the composite perovskite film. The PEG-doped CsPbBr₃ film also presents a much longer PL lifetime than that of the neat CsPbBr₃ film, which is revealed by the time-resolved PL spectra (Figure 4c). The average lifetime (τ_{ave}) extracted from the PL decay curve for the neat CsPbBr₃ film is about 5.03 ns, while the composite perovskite film has a significantly prolonged lifetime of 38.71 ns, which is over seven times longer than that of the neat CsPbBr₃ film (Table S2). According to eqs 1 and 2, which display the relationship between the radiative decay rate $k_{\rm r}$ and the nonradiative decay rate $k_{\rm nr}$

$$PLQY = k_r / (k_r + k_{nr})$$
⁽¹⁾

$$\tau = 1/(k_{\rm r} + k_{\rm nr}) \tag{2}$$

The nonradiative decay rate k_{nr} can be expressed as

$$k_{\rm nr} = (1 - \rm PLQY)/\tau \tag{3}$$

The PEG:CsPbBr₃ film shows a substantial reduced nonradiative decay rate of $\sim 1.68 \times 10^7 \text{ s}^{-1}$, which is 1 order of magnitude less than that of the neat CsPbBr₃ film ($\sim 1.97 \times 10^8 \text{ s}^{-1}$), further verifying that the addition of PEG effectively suppresses the surface defects or traps by passivating the perovskite crystals.

Because the Lewis base PEG would interact with the Lewis acid Pb^{2+} in $PbBr_2$, the chemical interaction between $PbBr_2$ and CsBr in the precursor solution would probably be influenced and thus affect the film formation states. We expect further improvement for the PeLED performance by optimizing the molar ratio of CsBr:PbBr₂ carefully. We investigated the variation in device performance with different CsBr:PbBr₂ molar ratios with or without PEG doping, which is plotted in Figure 5. For the devices without PEG doping, it is found that



Figure 5. Average values of the peak CE at different CsBr:PbBr₂ molar ratios. The error bar is estimated from at least six devices.

the maximum average CE remains at a low level less than 2 cd/ A as the CsBr:PbBr₂ molar ratio increases from 1.4:1 to 1.95:1, indicating that the CsBr passivation effect does not play a key role. In contrast to trivial changes in the maximum CE without PEG doping, the maximum average CE with PEG doping represents a conspicuous increment with the increased CsBr:PbBr₂ molar ratio and reaches a maximum average value of 18.2 cd/A at the CsBr:PbBr₂ molar ratio of 1.86:1, which is approximately 15 times higher than that of the device without PEG doping (maximum average CE of 1.18 cd/A). The detailed device parameters for the PEG-doped PeLEDs with different CsBr:PbBr₂ molar ratios are summarized in Table 2, the corresponding photos of the perovskite films exposed

Table 2. Summary of the EL Performance for PeLEDs with Different CsBr:PbBr₂ Molar Ratios at a Fixed PEG:CsPbBr₃ Weight Ratio of 0.034:1

CsBr:PbBr ₂ molar ratio	$\begin{array}{c} \text{max.} \\ \text{luminance} \\ \left(\text{cd}/\text{m}^2 \right) \end{array}$	max. CE (cd/A)	max. EQE (%)	turn-on voltage (V)	voltage @ max. luminance (V)
1.4:1	38900	4.26	1.20	2.8	5.8
1.54:1	36300	6.67	1.88	2.7	5.0
1.69:1	44700	8.86	2.49	2.6	5.2
1.77:1	40200	14.7	4.13	2.6	6.0
1.86:1	36600	19.0	5.34	2.5	5.2
1.95:1	25400	11.7	3.29	2.5	4.8

under UV light are listed in the inset of Figure 5, and the corresponding J-V, L-V, CE-V, and EQE-V are given in Figure S4. The optimized PeLED with a CsBr:PbBr₂ molar ratio of 1.86:1 shows a V_{on} of 2.5 V, a maximum luminance of 36600 cd/m² at 5.2 V, a maximum CE of 19.0 cd/A, and a maximum EQE of 5.34%. Moreover, the average lifetime for the PEG-doped CsPbBr₃ film with a CsBr:PbBr₂ molar ratio of 1.86:1 is further increased to 172.62 ns, approximately 21 times higher than that of the neat CsPbBr₃ film with the same CsBr:PbBr₂ molar ratio (Figure S5 and Table S2), indicating

significantly suppressed nonradiative decay and ensuring high device efficiency. As far as we know, among the reported inorganic PeLEDs with high brightness and high efficiency, our PeLEDs have the thinnest emission layers (Tables S3), which would be beneficial to reducing the self-absorption loss in PeLEDs and be a potential in preparing efficient transparent PeLED devices. Moreover, red PeLEDs based on CsPbBr_xI_{3-x} emitters with and without PEG doping were also prepared, and compared with the nondoping PeLED, the PEG-doped red PeLED presents significantly enhanced EL characteristics (Figure S6 and Table S4), which verifies the universal influence of PEG on PeLEDs.

In summary, the luminance and CE of inorganic PeLEDs with ultrathin emission films were successfully improved by the introduction of nonionic Lewis base PEG into the CsPbBr₃ perovskite emission layer. The ultrathin PEG:CsPbBr₃ layer (\sim 30 nm) reveals that two factors including the reduced crystal size of CsPbBr₃ and the passivated nonradiative defects mainly contribute to the dramatically enhanced EL performance. By further optimization of the molar ratio between CsBr and PbBr₂ in the precursor solution, greatly increased CE and EQE were obtained, reaching 19 cd/A and 5.32%, respectively, demonstrating the interaction between PEG and the precursor. The work therefore makes contributions to offering some useful suggestions to develop high-performance PeLEDs with ultrathin emission layers, which might have potential application in see-through displays.

EXPERIMENTAL METHODS

Materials. Lead(II) bromide (99.9%), cesium bromide (99.9%), PEDOT:PSS (poly(3,4-ethylenedioxythiophene)polystyreneulfonate) and TPBi (1,3,5-tris (2-*N*-phenylbenzimidazolyl)benzene) were purchased from Xi'an Polymer Light Technology Corp. PEG was purchased from Aladdin. All materials were used as received without further purification.

Film Fabrication and Characterization. The perovskite precursor solution was prepared by blending PbBr₂ and CsBr in anhydrous DMSO with a fixed concentration of 145 mg/mL. PEG was dissolved in DMSO with concentrations of 10, 15, and 18 mg/mL. The precursors and PEG solutions were mixed with desired weight ratios before use. For SEM (Hitachi S-4800) and AFM (Shimadzu SPA-9700) characterization, the perovskite films were spun on the ITO/PEDOT:PSS substrates (4000 rpm 60 s). The absorption spectra of the neat perovskite and PEG:CsPbBr3 composite films (on quartz substrates) were performed with a Shimadzu UV-3101PC UV-vis-NIR spectrophotometer. Fourier transform infrared (FTIR) spectra were recorded by a PerkinElmer FTIR spectrometer using KBr tablets. PL spectra were measured using Hitachi fluorescence spectrometer F-7000. Transient PL decay properties and absolute fluorescent quantum yield measurements were performed by an Edinburgh FLS920 spectrometer.

Device Fabrication and Characterization. Prior to device fabrication, transparent indium tin oxide (ITO) anodes were ultrasonically cleaned with acetone, alcohol, and deionized water in sequence and then treated with UV-ozone for 20 min. The PEDOT:PSS (Clevios P AI 4083) (~40 nm) was spin-coated on the ITO and baked at 140° for 20 min on a hot plate under ambient air. Then, the blend perovskite precursor:PEG solution was spin-coated at 4000 rpm for 60 s and annealed at 70° for 10 min in the N₂ filled glovebox. Subsequently, TPBi (30 nm), LiF (1 nm), and Al (60 nm) were successively thermally evaporated with rates of 1, 0.5, and 4 Å/s,

respectively. The brightness and current density of the PeLEDs were measured using a Keithley 2400 source meter and a luminance meter KONICA MINOLTA LS-110. The EL spectra were measured by an AvaSpec-ULS2048L fiber spectrometer. The EQE was calculated from the brightness, the current, and the EL emission spectrum assuming Lambertian emission. All measurements were carried out in air without encapsulation.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b01733.

AFM, EQE versus current density; XRD patterns, optical and electrical performance for PeLEDs with different CsBr:PbBr₂ molar ratios or for red PeLEDs, timeresolved PL decay curves, and additional tables (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by the CAS Innovation Program, the National Natural Science Foundation of China No. 51503196 and 61405195, the Jilin Province Science and Technology Research Project No. 20170101039JC, 20150101039JC, 20160520176JH, and 20160520092JH, and a project supported by the State Key Laboratory of Luminescence and Applications.

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