Red Perovskite Light-Emitting Diodes with Efficiency Exceeding 25% Realized by Co-Spacer Cations

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1. Introduction

Solution-processed metal halide perovskites have attracted considerable research interest as a new type of semiconductor materials, which has been utilized in solar cells, light-emitting diodes, and other optoelectronic devices.[1–8] In particular, perovskite light-emitting diodes (PeLEDs) have been conferred as the cutting-edge research due to their high performance, [9–16] red skite light-emitting diodes (PeLEDs) have been conferred as the highest performance for red PeLEDs up to now.

To date, the red PeLEDs have achieved significant external quantum efficiencies (EQE) that over 20%, most of them are based on the 3D and quantum-dot (QD) perovskite material.[17–22]

Compared with 3D and QD perovskite, quasi-2D perovskite would be more efficient emission material due to its higher exciton binding energy, multi-quantum-well structure, and good charge transfer properties.[23–28] Ruddlesden–Popper perovskite (RPP) is generally described by the formula of \( \text{La}_{a-1-b} \text{B}_{a} \text{C}_{x} \text{X}_{3x+1} \) as typical quasi-2D perovskites, which consist of large organic cation \( L \), a small organic or cesium cation \( A \), divalent metal cation \( B \) (lead or tin), and halide anion \( X \) (Cl\(^-\), Br\(^-\), or I\(^-\)). Although the overall development of red LED is remarkable, the quasi-2D red LEDs are still in arrears of efficiency. The reason may be that fine control of quasi-2D perovskite phase (represents the thickness of the \([\text{PbI}_6]^{2-}\) octahedra layers capped by the \( L \) cations)\(^{[28–31]} \) distribution is a great challenge, and random phase distribution will lead to the inferior charge injection and serious non-radiative recombination.

In this work, we report a general strategy of co-spacer cations to control the phase distribution in RPP films, by mixing a representative of phenethylammonium iodide (PEAI)/3-fluorophenylethylammonium iodide (m-F-PEA) and 1-naphthylmethylammonium iodide (NMAI) to alloy the RPP films. These RPP films show significant suppression of small index phase \((n = 2)\), and the carrier transport has been improved effectively. At the same time, the mixing of NMA can reduce the metallic Pb states and halide defects in RPP films, moreover, a smooth and pinhole-free perovskite film has been obtained. As a result, larger than 90% photoluminescence quantum yield (PLQY) is achieved through the mixing of m-F-PEA and NMA with a mixing ratio of 6:4, the LED prepared by this method achieves the efficiency as high as 25.8% and the maximum luminance of exceeding 1300 cd cm\(^{-2}\) at 680 nm.

2. Results and Discussion

We prepared RPP films of \((\text{PEA}_{x}\text{NMA}_{1-x})_{3}\text{CsPbI}_7\) and \((\text{m-F-PEA}_{x}\text{NMA}_{1-x})_{2}\text{CsPbI}_3\) with different composition \((x = 0, 0.2, 0.4, 0.6, 0.8, \text{and } 1)\) to study the effect of co-spacer cations on perovskite properties. The molecular structures of PEA,
m-F-PEA and NMA cations are shown in Figure 1a. m-F-PEA represents that a halide F atom is contained on the para-position on the conjugated phenyl ring in PEA. Among them, we found that the mixed cation perovskite with $x = 0.6$ is the optimized condition, which will be shown in the following. PEA cation only and cation mixture perovskites are expressed as P10N0, P6N4, and mFP6N4 in this study, where P means PEA, mFP means m-F-PEA, and N refers to NMA. Figure 1b represents UV–vis absorption spectra and steady photoluminescence (PL) spectra of the three films. The multiple absorption peaks suggest that thin perovskite films likely contain mixed quasi-2D structures with different $n$ values.\textsuperscript{[32,33]} The film P10N0 shows several strong exciton absorption peaks at \(\approx 560\) and \(\approx 610\) nm, corresponding to the phase of $n = 2$ and 3. While introducing NMA, the films of P6N4 and mFP6N4 absorption peaks corresponding to $n = 2$ and 3 are decreased significantly, and the peak of $n = 2$ is almost negligible in the mFP6N4 film. Consisting with the absorption, the film P10N0 shows obvious emission peaks of $n = 2$ and 3. And the films P6N4 and mFP6N4 mainly contain large $n$ phase, which lead to the redshifted PL spectra and no obvious emission of $n = 2$. The comprehensive UV–vis absorption spectra and PL spectra from quasi-2D perovskite films with different compositions (Figures S1 and S2, Supporting Information) confirm this trend. It must be noted, along with the redshift of PL for co-spacer cations, the full width at half maximum (FWHM) decreased from 43 to 34 nm, indicating that the phase distribution in quasi-2D perovskite become narrow. The weak PL intensity of P10N0 and P0N10 samples could due to the trap-assisted nonradiative recombination and strong electron–phonon coupling.\textsuperscript{[34–36]} We carried out PLQY measurements for these three films, as seen from Figure 1c, the PLQY of perovskite sample increases from 53\% (P10N0) to 78\% (P6N4) and 91\% (mFP6N4) while using co-spacer cations, and the targeted films exhibit strong emission under ultraviolet illumination (Figure S3, Supporting Information). Figure 1d shows the time-resolved photoluminescence (TRPL) decay profiles of different samples, with the mixing of NMA, the average PL lifetime of the quasi-2D film gradually increases from 5.321 (P10N0) to 8.308 (P6N4) and 8.523 ns (mFP6N4), suggesting the suppression of nonradiative recombination while engineering cations.

Figure 2a represents the X-ray diffraction (XRD) patterns of different quasi-2D perovskite films, the strong diffraction peak of $n = 2$ (2\(\theta = 3.8^\circ\)) can be observed in P10N0 film, indicating a dominant of small index of $n = 2$ phase. As NMA mixed with PEA/m-F-PEA, the peaks of $n = 2$ phase reduce significantly, and the large-$n$ phases become the main part in the P6N4 and mFP6N4 films. The slight shift of diffraction peaks of $n = 2$ is related to the crystal lattice change caused by the addition of the larger sized NMAI, which is further confirmed by the $n = 1$ phase 2D perovskites with different-sized organic cations (Figure S4, Supporting Information). Also, the presence of only one set of XRD patterns suggests that a single quasi-2D perovskite structure is formed for the perovskite with co-spacer cations. Compared with the (212) and (111) peaks in P10N0 film, the strong (110) and (220) peaks are observed from P6N4 and
mFP6N4 films, implying that the preferred orientation has been formed in the co-spacer cation perovskite. In addition, grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were performed to further investigate the crystal phase and crystallinity of the quasi-2D films, the Debye–Scherrer rings showed in P10N0 films indicate a random crystalline orientation, while stronger scattering spots along the q_z direction are exhibited in P6N4 and mFP6N4 indicating a vertical alignment of (110) with respect to the substrate (Figure 2b–d), which facilitates the charge vertical transport.\textsuperscript{[37–39]} The crystallinity of perovskite with different crystal planes collected by high-resolution transmission electron microscopy (HRTEM) is shown in Figure 2e,f. For the P10N0 film, the n = 2 phase crystal planes in P10N0 can be clearly observed, the crystal plane of (212) and (111) from large-n phase (close to 3D perovskite) are also found in Figure S5, Supporting Information. While for the co-spacer cation films, the dominant (110) crystal plane with good crystallization were observed, consistent with our finding in the XRD results.

Time-resolved transient absorption (TA) measurements were carried out to derive the phase distribution and energy funnel process in quasi-2D perovskite films. For the P10N0 film, as seen from Figure 3a,d, there are several ground-state bleaching (GSB) peaks around 560, 610, 635, 655, and 670 nm, which correspond to the phase of n = 2, 3, 4, 5, and n ≥ 6 in RPP film and represent the evolution of excited-states carriers, respectively.

It can also be found that the photogenerated carriers are initially formed in the wide-bandgap quantum well of n = 2 phase, while the charge transfer process from n = 2 phase to large-n phase is more than 100 ps based on the absorption bleaching results, which could retard carrier concentration and reduce radiative recombination in the emitting center (large-n phases).\textsuperscript{[29]} For the co-spacer cation films, as shown in Figure 3b,e and 3c,f, the peaks of different phases still exist, the most significant difference is that the peak of n = 2 phase is almost negligible after attenuation of about 1 ps, indicating much faster charge transfer happened in the quantum well structure for the co-spacer cation system.

Figure 2. Microstructure of quasi-2D films with different compositions. a) XRD pattern of P10N0, P6N4, and mFP6N4 films. b–d) GIWAXS maps of P10N0 (b), P6N4 (c), and mFP6N4 (d). e–g) HRTEM images of n = 2 phase in P10N0 (e), (110) in P6N4 (f), and (110) in mFP6N4 (g).
To further study the energy transfer process, the kinetics of each GSB are fitted by a function that includes a fast decay component $\tau_1$ related to the carrier transferring from small-$n$ phase to large-$n$ phases in perovskite film, slow decay components $\tau_2$ and $\tau_3$ related to the energy decay and recombination, and the rapid increase component $\tau_{et}$ related to the establishment of GSB peak.\textsuperscript{40,41} Figure 3g–i shows the decay kinetics about different phases of three perovskite films, the results of fitted lifetime components are given in Table S1, Supporting Information. The fast decay time $\tau_1$ of $n=2$ and $n=3$ phases in P10N0 film are 0.44 and 0.19 ps, respectively, then the excitons continuously transferred to $n \geq 6$ phases for the radiative recombination. Encouragingly, the fast decay time $\tau_1$ of $n=2$ phase in P6N4 (0.05 ps) and mFP6N4 (0.05 ps) are nine times shorter than that in the pristine one, with $\tau_1$ of $n=3$ phase in P6N4 (0.10 ps) and mFP6N4 (0.10 ps), which are two times shorter than that in P10N0. The shorter $\tau_1$ means that the carriers are transferred out of the quantum well at a faster rate.\textsuperscript{25} Meanwhile, the establishment time $\tau_{et}$ of the emission phase for P10N0, P6N4, and mFP6N4 is 1.21, 1.10, and 1.02 ps, respectively. The above results show that the co-spacer cation strategy can effectively improve the energy transfer process in the perovskite films.

X-ray photoelectron spectroscopy (XPS) measurements were performed to check the effect of the co-spacer cations on the chemical states of the elements in the perovskite. The core levels of Pb 4f\textsubscript{7/2} from the three different compositions of perovskite are shown in Figure 4a–c. The dominant peak around 138 eV is corresponding to the Pb–I bond in [PbI\textsubscript{6}]\textsuperscript{4–}, and the shoulder peak around 136 eV corresponds to metallic Pb states. For the control film, an obvious Pb metallic state can be easily found, which is detrimental to the PeLED performance due to the serious non-radiative recombination.\textsuperscript{3} After mixing the PEA with NMA, the metallic Pb peak becomes weak but still exist, and it is very encouraging that the metallic Pb peak is fully suppressed in mFP6N4 system. The reduction of metallic Pb states could be one of main reasons for the high PLQY for the co-spacer cation system.
In addition to the suppression of metallic Pb states, we also found that there are some chemical shifts for the I core level. Compared with P10N0 and P6N4, the core level of I in mFP6N4 exhibits a blueshift of 0.2 eV (Figure S6, Supporting Information), means the stronger interaction between I and Pb and a more stable crystal structure.[42,43] The main effect could be due to the substitution of fluorine for hydrogen on the benzene ring of PEA, which will change the electronic structure of the molecule, then resulting slight differences in octahedral tilting, shorter average phenyl ring centroid–centroid distances and more tightly stacked perovskite sheets.[42–45] Meanwhile, the electron withdrawing of F atom could suppress the formation of halide dangling bonds.[21]

Scanning electron microscopy (SEM) was used to investigate the surface morphology of thin quasi-2D perovskite films, as shown in Figure 4d–f and Figure S7, Supporting Information. Noticeably, the P10N0 perovskite film shows some isolated large grains, while obvious pinholes are observed from both P10N0 and P0N10 samples. These features could be detrimental to achieving high device performance due to the current leakage. We found that the co-spacer cations could effectively reduce the pinhole and suppress the formation of large isolated particles, and it is very encouraging that the perovskite film becomes very dense and continuous while mixing m-F-PEA and NMA. In previous studies, it has been reported that low-dimensional perovskite tends to aggravate the formation of larger grains and rougher perovskite films, due to the existence of layer perovskite phases.[40,41] This study has confirmed that the strategy of co-spacer cations can reduce the small index of quasi-2D perovskite, which guarantees the formation of smaller grains and reduces the surface holes and defects of perovskite. Atomic force microscopy (AFM) results also confirmed the better morphology while mixing m-F-PEA with NMA (Figure S8, Supporting Information), the root mean square roughness of three perovskite films decreased from 6.29 (P10N0) to 5.30 (P6N4) and 2.64 nm (mFP6N4).

We fabricate the perovskite films into configure LEDs based on device structure of ITO/the modified PEDOT:PSS (m-PEDOT: PSS) (40 nm)/poly-TPD (poly(N,N′-bis(4-butylphenyl)-N,N′-bis(phenyl)-benzidine)) (10 nm)/PVK (poly(9-vinylcarbazole)) (5 nm)/quasi-2D perovskite (50 nm)/TPBi (2,2′,2′′-(1,3,5-benzinetriyl)-tris(1-phenyl-1H-benzimidazole)) (30 nm)/LiF (1 nm) Al (100 nm). Figure 5a shows a schematic of the flat-band energy-level diagram of the multiple layers. The cross-sectional SEM image of devices is shown in Figure 5b, and a clear sandwich structure is clearly observed. The electroluminescence performance of PeLEDs with different ratios of m-F-PEA and NMA indicates that the mFP6N4 is the optimum composition (Table S2, Supporting Information). The typical EL spectra of P10N0, P6N4, and mFP6N4 are shown in Figure 5c. Although the quasi-2D perovskite films exhibit a mixture of many phases with different bandgaps, only a single red EL peak is observed. Compared with the peak of P10N0 (~660 nm), the peaks of P6N4 and mFP6N4 (~680 nm) have a slight redshift, which is consistent with the PL results (Figure 1a).

According to the current density–voltage–luminance (J–V–L) plot (Figure 5d), the leakage current of the P10N0 film is obviously higher than that of films with co-spacer cations, but the subsequent injection current is lower, indicating that there is a higher defect density in P10N0 films and the redundant n = 2 phase will hinder the injection of current.[46] Furthermore,
it could be found that the leakage current of P6N4 is slightly higher than that of mFP6N4, which consists with that mFP6N4 owns better morphology. In Figure 5e, it is apparent that the performance of the devices with co-spacer cations is better than that of the device with single organic cation, a very high EQE value of 24.2% is achieved with a luminance of 1300 cd m$^{-2}$ in mFP6N4 film, while just 19.7% with 850 cd m$^{-2}$ in P6N4 and 11.6% with 400 cd m$^{-2}$ in P10N0, and the maximum EQE of champion PeLED based on mFP6N4 could reach 25.8% (Figure 5f). In addition, the result of EL performance with different mixing ratio of m-F-PEA and NMAI is shown in Table S2, Supporting Information. The EL spectrum of the device under different voltages is given in Figure S9, Supporting Information. As the bias voltage increases, the device shows good spectral stability and also with nice EL performance at Commission Internationale de l’Eclairage (CIE) coordinates of (0.722, 0.277) (Figure S10, Supporting Information). We also collected the EQE data for 27 devices, the device shows only 5.1% relative deviation (Figure S11, Supporting Information), demonstrating the good reproducibility of the co-spacer cation strategy. In addition to increase the device efficiency, we also found that the co-spacer cation method improves the operational stability. The $T_{50}$ operational time was increased to over five times with an initial brightness of 100 cd m$^{-2}$ (Figure S12, Supporting Information), which is due to the passivation of the defects in the perovskite layer (Figure 3a–c) and the increased interaction between I and Pb. In order to further improve the operational stability, the device structure needs to be optimized to decrease the resistance and reduce the degradation caused by Joule heat. It is also necessary to improve the maximum luminance of the device and cut down the injection current at 100 cd m$^{-2}$ in the future studies.
3. Conclusion

Co-spacer cation quasi-2D (PEA/m-F-PEA)₂NMA₁₋₂,₃⁻CsPb₂I₇ RPP films were developed for efficient red PeLED. Low-dimensional films were passivated. Accordingly, efficient red PeLED with a maximum EQE of 25.8% at 680 nm is achieved. Our method provides a strategy to control phase distribution and passive defects simultaneously, which is beneficial to realize more efficient PeLEDs and could also be good for solar cells.

4. Experimental Section

Materials: CsI, PbI₂, LiF, dimethyl sulfoxide (DMSO), ethyl acetate (EA), chlorobenzene, and poly (sodium 4-styrenesulfonate) (PSS-Na, average Mₙ = 70 000) were purchased from Sigma-Aldrich. TPBi, PEAI, m-F-PEA, NMAI, and PVK (average Mₙ > 100 000) were purchased from Xi’an Polymer Technology Corp. Poly-TPD was purchased from 1-Material. And the m-PEDOT:PSS solution was a mixture of normal PEDOT:PSS (Al 4083) aqueous solution with 100 mg mL⁻¹ PSS-Na aqueous solution by a volume ratio of 6:5.

Perovskite Precursor Synthesized: The quasi-2D perovskite (PEA)₂CsPb₂I₇ precursor was prepared by dissolving PEAI, CsI, and PbI₂ in a molar ratio of 1:0.75:1 in DMSO under continuous stirring overnight at 40 °C, keeping the molar concentration Pb²⁺ at 0.5 M and the ((PEA/m-F-PEA)₁₋₂,₃⁻NMA₁₋₂,₃⁻CsPb₂I₇ precursor was prepared by mixing PEAI/m-F-PEA and NMA in a molar ratio of 1:1 on the basis of single-cation perovskite (x = 0, 0.2, 0.4, 0.6, 0.8, and 1).

Device Fabrication: Indium tin oxide (ITO)-coated glass substrates were sequentially cleaned in detergent, deionized water, acetone, isopropyl alcohol. Then dried it with nitrogen and treated it with UV ozone for 20 min. The m-PEDOT:PSS aqueous solution was spin-coated at 7000 rpm for 40 s, followed by drying at 160 °C for 15 min in ambient air. Then, the samples were transferred into a nitrogen-filled glovebox, spin-coating poly-TPD (10 mg mL⁻¹ in chlorobenzene) and PVK (2.5 mg mL⁻¹ in chlorobenzene) on the m-PEDOT:PSS substrate at 2000 rpm for 40 s in turn, and annealing at 150 °C for 30 min. The RPP films were fabricated by spin-coating the precursor solutions at 9000 rpm for 60 s, and after spin-coating for 15 s, 120 µL of EA was poured onto the film as an anti-solvent, followed by annealing at 80 °C for 15 min. Finally, the TPBi layer (30 nm) and LiF/Al electrodes (1 nm/100 nm) were deposited through a shadow mask in a high vacuum of ~1 × 10⁻³ Pa thermal evaporator. The device active area was 0.1 cm² as defined by the overlapping area of the ITO and Al electrode.

Film and Device Characterization Measurement: Absorption spectra were measured using a UV–vis spectrometer (Cary 5000). PL spectra and TRPL were acquired at room temperature in the ambient air using an FLS1000 spectrometer with excitation at 375 nm from a 450 W xenon lamp. The XRD patterns of the perovskite (x=0,0.2,0.4,0.6,0.8,1) thin films were performed with a Rigaku D/max 2500H equipment with excitation from a 368 nm LED. The XRD patterns of the perovskite on the basis of single-cation perovskite were measured using a X’pert PRO Panalytical X-ray diffractometer (X’pert PRO, Panalytical) with Cu Kα radiation (λ = 1.5405 Å), with X-ray spot to analyze XPS while the analysis chamber background pressure of ~1 × 10⁻¹⁰ mbar. Typically, the hydrocarbon C 1s line is formed from amorphous carbon at 284.8 eV for reference energy. AFM measurements were carried out by an NT-MDT Solver P47 AFM in a semi-contact mode. The SEM images were carried out by a field-emission SEM (FEI NanoSEM650), which was used an electron beam accelerated at 500 V to 30 kV. TEM was carried out with a JEOL JEM-2100F, operated at 200 kV. The EQE, J–V–L curve, EL spectrum, CIE, and operating lifetime of the perovskite LED were carried out simultaneously by a commercialized system (LQE-50-EL, Enlitech) with an integrated sphere and photomultiplier tubes (PTM), which was used to measure the low lumiance, and all electrical tests were conducted at room temperature in the ambient air for the un-encapsulated devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

cospace cations, electroluminescence, light-emitting diodes, quasi-2D perovskites

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