

Hole Transport Bilayer Structure for Quasi-2D Perovskite Based Blue Light-Emitting Diodes with High Brightness and Good Spectral Stability

Zhenwei Ren, Xiangtian Xiao, Ruiman Ma, Hong Lin, Kai Wang, Xiao Wei Sun, and Wallace C. H. Choy*

Substantial achievements have been made in green and red perovskite light emitting diodes (PeLEDs) recently. However, blue PeLEDs still lag behind with much lower performances. One of the main reasons is the mass undesirable nonradiative recombination at interfaces and within the perovskite films. In this work, an efficient hole transport bi-layer structure composed of PSSNa and NiO_x is demonstrated to simultaneously inhibit the nonradiative decays between NiO_x and perovskite films by reducing NiO_x surface defects and improving quasi-2D perovskite thin film quality by minimizing its pin-holes and reducing the film roughness. The results show that the dipole feature of PSSNa improves the hole transportation and thus PeLED performances. Moreover, by introducing KBr into the perovskite, its film quality improves and trap states reduce. Eventually, the blue PeLEDs is achieved with a very low turn-on voltage of 3.31 V accompanied with an external quantum efficiency of 1.45% and a remarkable luminance of 4359 cd m^{-2} . With further optimization of the perovskite precursor concentration, the highest luminance reaches 5737 cd m^{-2} , which represents the brightest blue PeLEDs reported to date as far as it is known. Furthermore, the devices also show better spectral stability and operation lifetime as compared to other blue PeLEDs.

1. Introduction

Metal halide perovskites have emerged as an attractive class of semiconductors with simple solution processability for green-energy optoelectronics.^[1–6] More recently, the perovskites based light-emitting diodes (PeLEDs) have promoted considerable research efforts due to the excellent features in wide tunable bandgaps, high color purity and photoluminescence, facile synthesis, and low materials cost.^[7–11] Of particular interests

are green, red, and near-infrared light-emitting PeLEDs which have achieved great improvements.^[12–22] However, for blue PeLEDs, it remains a big challenge to obtain the comparable performance.

In order to obtain the blue spectrum of electroluminescence (EL), the halogen component of the perovskites can be chosen as monotonic Cl or tuned with mixed Br and Cl anions.^[23–25] However, the emission profiles shift with increasing driving voltages owing to either the poor stability of pure Cl-perovskites or migration of the halogen ions in the mixed perovskites.^[26] In addition, in situ passivation of PbBr_6^{4-} octahedra in CsPbBr_3 nanoplatelets was also proved to be an effective strategy to acquire high photoluminescence quantum yield (PLQY) for blue emission, in which near 100% absolute quantum yield was achieved. However, the constructed blue PeLEDs only show the maximum external quantum efficiency of 0.124% indicating a lot of opportunities for further improvement

on electroluminescent properties and efficiency.^[27] Quasi-2D perovskites with reduced stacking numbers of perovskite unit cells exhibit a large extent of blueshift.^[28–30] Meanwhile, the assembled multiple-quantum-well structure in quasi-2D perovskites can facilitate the formation of excitons and reduce the possibility of exciton dissociation.^[28,31] The first low-dimensional perovskite LED was demonstrated to give a visible emission by controlling the ratio of methyl ammonium to phenylethyl ammonium.^[32] Later, randomly oriented nanocrystals were introduced by the modified nanocrystal pinning for further improving the PeLED performance.^[33] Consequently, it is highly desirable to use quasi-2D perovskites for constructing efficient blue PeLEDs.

Recently, significant works have been done to optimize the performances of blue PeLEDs. For example, aryl and alkyl ammoniums of 2-phenoxyethylamine,^[34] 4-phenylbutylamine,^[35] butylammonium bromide,^[36,37] and ethylammonium bromide^[38] have been introduced into 3D $\text{CH}_3\text{NH}_2\text{PbBr}_3/\text{CsPbBr}_3$ perovskites. Meanwhile, different amounts of ammoniums were carefully investigated to obtain high device performances for quasi-2D blue PeLEDs. In order to control the formation of quasi-2D perovskites with the desired phase,

Dr. Z. Ren, X. Xiao, R. Ma, Dr. H. Lin, Prof. W. C. H. Choy
Department of Electrical and Electronic Engineering
The University of Hong Kong
Pokfulam Road, Hong Kong 999077, China
E-mail: chchoy@eee.hku.hk

X. Xiao, Prof. K. Wang, Prof. X. W. Sun
Department of Electrical and Electronic Engineering
Southern University of Science and Technology
Shenzhen 518055, China

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adfm.201905339>.

DOI: 10.1002/adfm.201905339

mixed ammoniums were employed. The blue PeLEDs with the luminance of 2480 cd m^{-2} , peak wavelength of 490 nm, and external quantum efficiency (EQE) $<1\%$ were demonstrated.^[39] Subsequently, the Cl-doped quasi-2D perovskites were adopted in blue PeLEDs, and the luminance was further improved to 3780 cd m^{-2} . However, there is a concern in the phase separation in the perovskite films which will cause the unstable nature of electroluminescence spectra.^[40] Besides, by reducing the trap states of perovskites through adding a proper amount of manganese dopant, PeLEDs with the EQE of 2.12%, luminance of 245 cd m^{-2} , and peak wavelength of 466 nm were reported.^[41] Furthermore, except for the improvements of perovskites, adopting a suitable carrier (hole and electron) transport/injection layer to reduce carrier injection barrier^[42–45] is another way to improve the performance of blue PeLEDs. For example, NiO_x was widely used as an efficient hole transport layer (HTL) in perovskite photovoltaics attributed to the matched band alignment for hole extraction.^[46–50] However, NiO_x HTL has been limitedly studied in blue PeLEDs because of the mass nonradiative decay channels at the interface layers.^[51] The previous NiO_x film based blue PeLEDs exhibit relatively weak luminance of 350 cd m^{-2} and EQE of 0.07%.^[24] With combination of NiO_x/LiF , the recent luminance and EQE have been increased to 1446 cd m^{-2} and 0.52%,^[52] respectively. However, there is a concern of the diffusion of Li ions in the device structure,^[53] which may change the PeLED performances. Meanwhile, it is necessary to further improve the emission properties of blue PeLEDs for their practical applications.

In this work, we propose to introduce a thin polymer layer of poly(sodium-4-styrene sulfonate) (PSSNa) on NiO_x for forming a bilayer HTL structure for quasi-2D PeLEDs. Through adding PSSNa, we target to simultaneously suppress the nonradiative recombination through the reduction of defect states in NiO_x films, and improve the morphology of perovskite film by reducing the film roughness and minimizing the pinholes. In addition, a lower valance band is also demonstrated in the bilayered structure which benefits from the dipole feature of PSSNa for efficient hole injection. Meanwhile, in order to further improve the 2D perovskite film quality, we incorporate KBr into the quasi-2D perovskite for inhibiting the nonradiative losses by passivating the traps in the perovskite films. Finally, the optimized blue PeLEDs exhibit an impressive luminance of 4359 cd m^{-2} (further improved to 5737 cd m^{-2} by optimizing the perovskite precursor concentration), a very low turn-on voltage of 3.31 V, and an EQE of 1.45%. The optimized luminance represents the brightest blue PeLEDs reported to date from our best knowledge. Furthermore, the devices also show better spectral stability and operation lifetime as compared to other blue PeLEDs.

2. Results and Discussion

2.1. Formation of Bilayer NiO_x -PSSNa Films

The well-dispersed and ligand-free NiO_x nanoparticles (NPs) with an average crystallite size of $\approx 4 \text{ nm}$ were synthesized through the previous reported facile chemical precipitation method.^[54] The NiO_x films were obtained by spin-coating the NP solution with the optimized concentration. The bilayer

NiO_x -PSSNa films were fabricated by spin-coating PSSNa methanol solution on NiO_x films. The perovskite films were prepared by spin-coating the precursor solution of dimethyl sulfoxide (DMSO) followed by an antisolvent process with toluene. Details are discussed in the Experimental Section. The morphology of NiO_x , NiO_x -PSSNa, and DMSO-washed NiO_x -PSSNa films were characterized by atomic force microscope (AFM) as shown in Figure S1 (Supporting Information). The surface roughness (R_q) of NiO_x -PSSNa film was smaller than that of NiO_x film, indicating the film smoothening function by PSSNa treatment. In addition, the value of R_q for DMSO-washed NiO_x -PSSNa film is close to the unwashed film, which maintains smaller than that for untreated NiO_x film. This illustrates that PSSNa cannot be washed away by the solution of perovskite due to the undissolved feature of PSSNa in DMSO solvent. The thickness of NiO_x and PSSNa layers are ≈ 20 and $\approx 2 \text{ nm}$, respectively, which were estimated by profilometer.

2.2. High-Quality Perovskite Films Obtained from the Bilayer HTL

To explore the quality of perovskite emission layer deposited on NiO_x and NiO_x -PSSNa films, scanning electron microscope (SEM) and AFM measurements are carried out. As shown in Figure 1a,d, when the perovskite was directly formed on NiO_x film, large amounts of pinholes with different sizes have appeared. Interestingly, this issue can be addressed by forming a thin layer of PSSNa in-between NiO_x and the perovskite. The density of pinholes is greatly minimized and the surface roughness is moderately reduced from 5.35 to 3.67 nm, so that a more uniform perovskite film is realized (Figure 1b,e). This can be explained by the better wetting of perovskite precursor solution onto NiO_x -PSSNa film (Figure S2, Supporting Information). It is also noted that the improvement of wettability is well maintained in the DMSO-washed NiO_x -PSSNa film, which indicates that the thin PSSNa layer cannot be removed by DMSO. This result is in very good agreement with the AFM results (Figure S1, Supporting Information), demonstrating the important roles of PSSNa layer for preparation of high-quality perovskite films by reducing the pinholes and surface roughness. Furthermore, when KBr was introduced into the quasi-2D perovskite, the perovskite film with better morphology uniformity was prepared onto NiO_x -PSSNa film, which can be further revealed by the corresponding AFM measurement (Figure 1f), the roughness was significantly decreased from 3.67 nm (without KBr additive) to 2.56 nm (with KBr additive) showing the smoother perovskite surface. Equally important, the average grain size of KBr decorated perovskite increases from $\approx 57 \text{ nm}$ of pure perovskite (Figure 1b) to $\approx 66 \text{ nm}$ (Figure 1c). Although the introduction of KBr into 3D perovskites has been reported,^[55–57] there is very limited studies of the incorporation of KBr into quasi-2D perovskite. Our results show the improved quasi-2D perovskite quality owing to the potassium ion promoted growth process of perovskites. The potassium in the quasi-2D perovskites was determined by energy-dispersive X-ray spectroscopy (EDS) element mapping which showed a well distribution of potassium in KBr decorated perovskite films (Figure S3, Supporting Information). The element content of

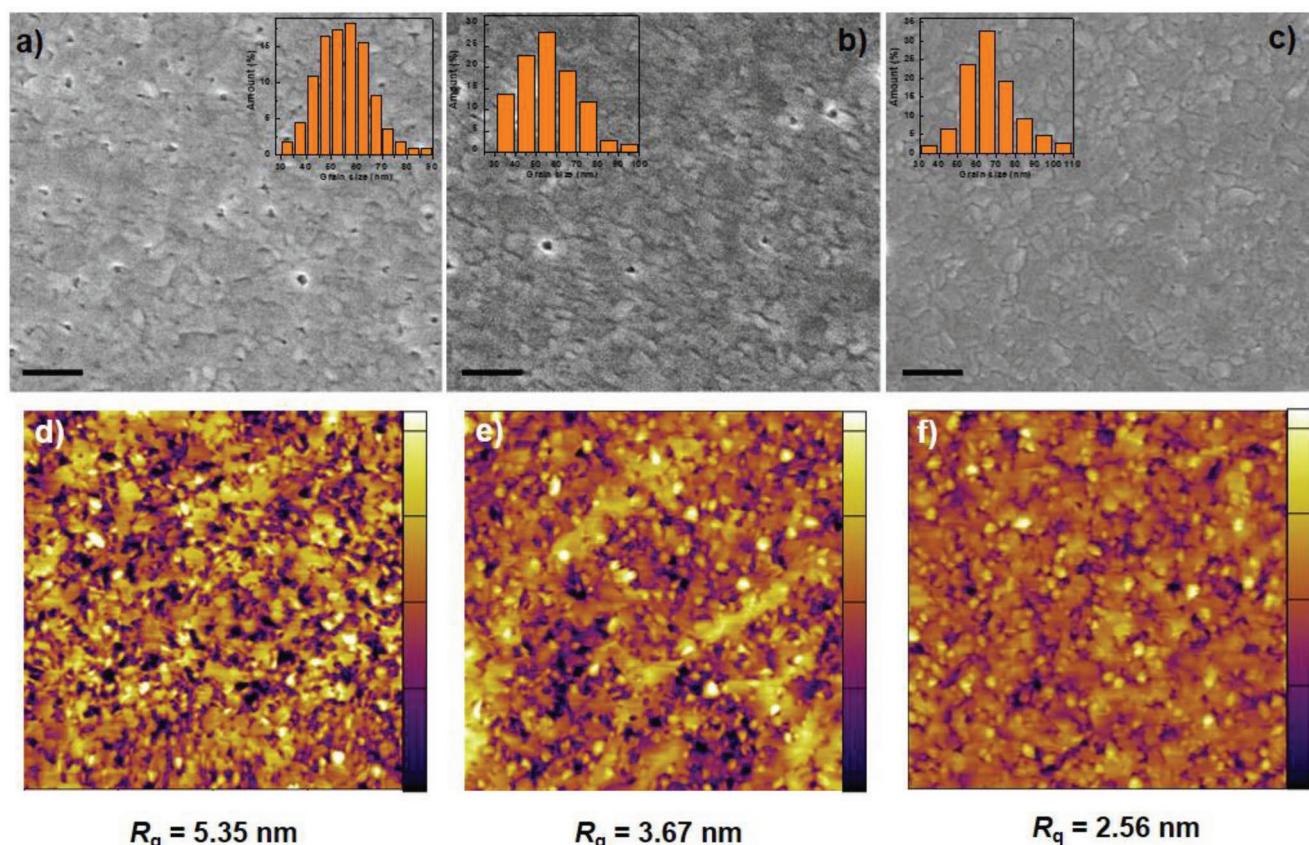


Figure 1. The scanning electron microscopy images and atom force topology of perovskite films: a,d) perovskite on NiO_x , b,e) perovskite on NiO_x -PSSNa, and c,f) perovskite with KBr additive on NiO_x -PSSNa films. The scale bars in SEM images are 200 nm, the AFM image sizes are $2 \times 2 \mu\text{m}$, and the corresponding scale bars are 22 nm (the distribution of perovskite grain size is shown in the inset of each SEM image).

potassium in the perovskite films was also recorded by the EDS spectrum (Figure S4, Table S1, Supporting Information), which shows a good agreement of potassium content with that in precursor solution. The characterizations also indicate that KBr is not released into the air during spin-coating. From the SEM images (Figure 1b,c), we can see that high quality of the perovskite has been achieved with the incorporation of KBr. To further study the effect of KBr on the crystallization of the perovskite, the X-ray diffraction (XRD) measurements are performed (Figure S5, Supporting Information). It is found that the diffraction peak intensity of KBr decorated perovskite is much stronger than that of the pristine perovskite, which suggests that KBr can favor the perovskite crystallization and increase the crystallinity. The mechanism how KBr improves the perovskite film quality is possibly related to crystallization kinetics, in which KBr could slow down the crystallization process to make perfect perovskite crystals. As it is known that the metal ions can promote growth process of perovskites for high crystallization, which is an efficient way to achieve high quality of perovskite films.^[55] Consequently, by introducing the NiO_x -PSSNa bilayer structure, we can improve the quality of the quasi-2D perovskite by reducing its pinholes and smoothing its morphology. Together with the incorporation of KBr, high-quality (without pinholes, smooth morphology, and grain-size enhanced) quasi-2D perovskite films are achieved.

2.3. Nonradiative Recombination Reduction of Bilayer HTL/Perovskite Structure

The optical properties of the perovskite films are illustrated in Figure 2. Figure 2a shows the UV-visible absorption spectra of the perovskites formed on NiO_x and NiO_x -PSSNa films, and KBr decorated perovskite on NiO_x -PSSNa film which is hereafter named as NiO_x -PSSNa-KBr perovskite. Their corresponding steady-state photoluminescence (PL) is shown in Figure 2b. It is revealed that the pristine perovskite directly formed on NiO_x film shows weak intensity of PL with the emission peak wavelength of 488 nm. The photoluminescence quantum yield of perovskite deposited on NiO_x film was also measured, which exhibits a low PLQY of 9.8%. When the pristine perovskite films are deposited on NiO_x -PSSNa film, there is a remarkable increase in PL intensity without any shift in the emission spectrum, and the corresponding PLQY is increased to 12.7%. The dramatic enhancement of PL intensity is ascribed to the large reduction of nonradiative recombination, which benefits from not only the better film morphology but also the reduced surface traps at the interface between perovskite and NiO_x films by the insertion of PSSNa layer. The reduction of surface traps of NiO_x film can be confirmed by the improved PL intensity and carrier lifetime for PSSNa-modified NiO_x film as shown in Figure S6 (Supporting Information). For the perovskite decorated with

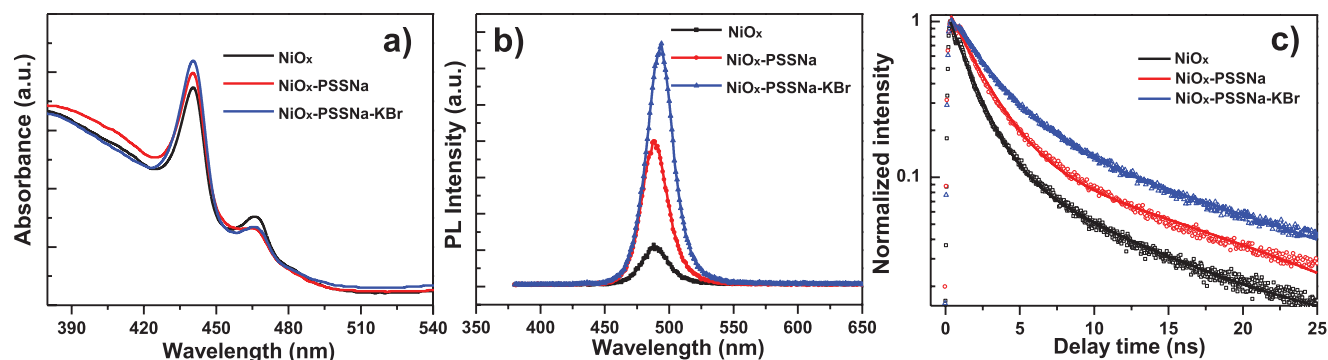


Figure 2. a) UV-vis absorption spectra, b) PL, and c) TRPL spectroscopy of the perovskites based on NiO_x and NiO_x-PSSNa films, and perovskite with KBr additive based on NiO_x-PSSNa film.

KBr additive, the PL intensity is further improved accordingly (see Figure 2b) and the value of PLQY increases to 18.7%. The stronger PL intensity indicates the less nonradiative recombination of NiO_x-PSSNa-KBr film, which benefits from the reduced trap states through potassium passivation at perovskite grain boundaries and surfaces^[55,56] as well as the enlarged grain sizes (i.e., better crystallization of the perovskite) as described before. The trap state density of KBr decorated perovskite film is considerably reduced by over 65% as compared to the pristine perovskite from $3.95 \times 10^{18} \text{ cm}^{-3}$ (pristine perovskite) to $1.38 \times 10^{18} \text{ cm}^{-3}$ (KBr decorated perovskite) (see Figures S7 and S8, Supporting Information). Although the origin of the trap states is not clear, they are widely believed to be caused by the ionic defects such as halide vacancies. The introduced potassium at perovskite grain boundaries and surfaces can anchor the bromide ions and inhibit bromide migration, which suppresses the halide vacancies and reduces the trap states.^[56] In addition, to better compare the PL peak positions of the perovskite films, the PL spectra have been normalized as shown in Figure S9 (Supporting Information). It is found that a slight redshift ($\approx 5 \text{ nm}$) was presented in the emission peak of KBr decorated perovskite film (493 nm), which can be ascribed to the slightly increased perovskite size induced by KBr. Besides, we also find that there is an enhanced dielectric confinement for KBr decorated perovskite (see Figure S8, Supporting Information). The dielectric constant of KBr doped perovskite is 11.45, which is smaller than the pristine perovskite (12.89). This means the dielectric confinement would be significantly enhanced for KBr decorated perovskite, which is associated with the large exciton binding energy (E_b)^[58–60] as further characterized in Figure S10 (Supporting Information). Thus, a reduced maximum optical bandgap (E_{opt}) is expected with the enlarged E_b , as shown in Figure S11 (Supporting Information). Subsequently, a slight redshift was found in the emission peak of KBr decorated perovskite film.

To further study the processes of carrier recombination in different perovskite films, we have studied time-resolved photoluminescence (TRPL) as shown in Figure 2c. The decays can be fitted by biexponential curves, in which the fast and slow decay components can be explained by the trap-assisted recombination at grain boundaries/interfaces, and radiative recombination inside the perovskite, respectively.^[16,61,62] The extracted parameters from the fitted curves are listed in

Table S2 (Supporting Information). It is shown that both of the fast and slow decay lifetimes for perovskite deposited on NiO_x-PSSNa film (τ_1 , 2.03 ns; τ_2 , 16.49 ns) are much higher than that on NiO_x film (τ_1 , 1.47 ns; τ_2 , 8.27 ns) revealing suppression of the exciton recombination caused by the traps at interfaces, and the bulk defects inside perovskite phase. When the perovskite is decorated with KBr, the fast decay component is further increased from 2.03 to 2.58 ns, while with a slight improvement of slow decay component from 16.49 to 16.52 ns. This is because that the additive of potassium mainly passivates the defects at perovskite grain boundaries and surfaces, which will be further discussed in the following parts. Benefiting from the contributions of PSSNa and KBr, the longer carrier lifetime corresponding to the higher PL intensity is achieved for NiO_x-PSSNa-KBr film which promotes an enhancement for high-performance PeLEDs. Overall, the static and transient PL studies together with the crystallization studies of the quasi-2D perovskites show that the introduced NiO_x-PSSNa bilayer structure effectively inhibits the nonradiative recombination at the interface between perovskite and NiO_x films. Along with the reduced trap states in quasi-2D perovskites by the decoration of KBr, we can further minimize the nonradiative recombination in NiO_x-PSSNa-KBr film, all of which pave a good way for applications in PeLEDs.

2.4. Device Structure and Performance

The PeLEDs with structure of ITO/NiO_x/PSSNa/PA₂(CsPbBr₃)_{*n*-1}PbBr₄/TPBi/LiF/Al have been investigated. The schematic illustration and the cross-section SEM image of the device are shown in Figure 3a,b, respectively. The optimized thicknesses of NiO_x-PSSNa, quasi-2D perovskite of PA₂(CsPbBr₃)_{*n*-1}PbBr₄, TPBi, and LiF/Al layers are about 22, 35, 50, and 100 nm, respectively. The PeLEDs with pristine NiO_x and pristine perovskite are also fabricated for comparison. The energy band of NiO_x with and without PSSNa layer, as well as the pristine and KBr decorated perovskite were determined by ultraviolet photoelectron spectroscopy (UPS) (see Figure S12, Supporting Information), and the calculated energy levels are shown in Figure 3c. The NiO_x-PSSNa bilayer films show lower energy level as compared to that of NiO_x film. This can be explained by the formation of molecular dipole moment (μ) by

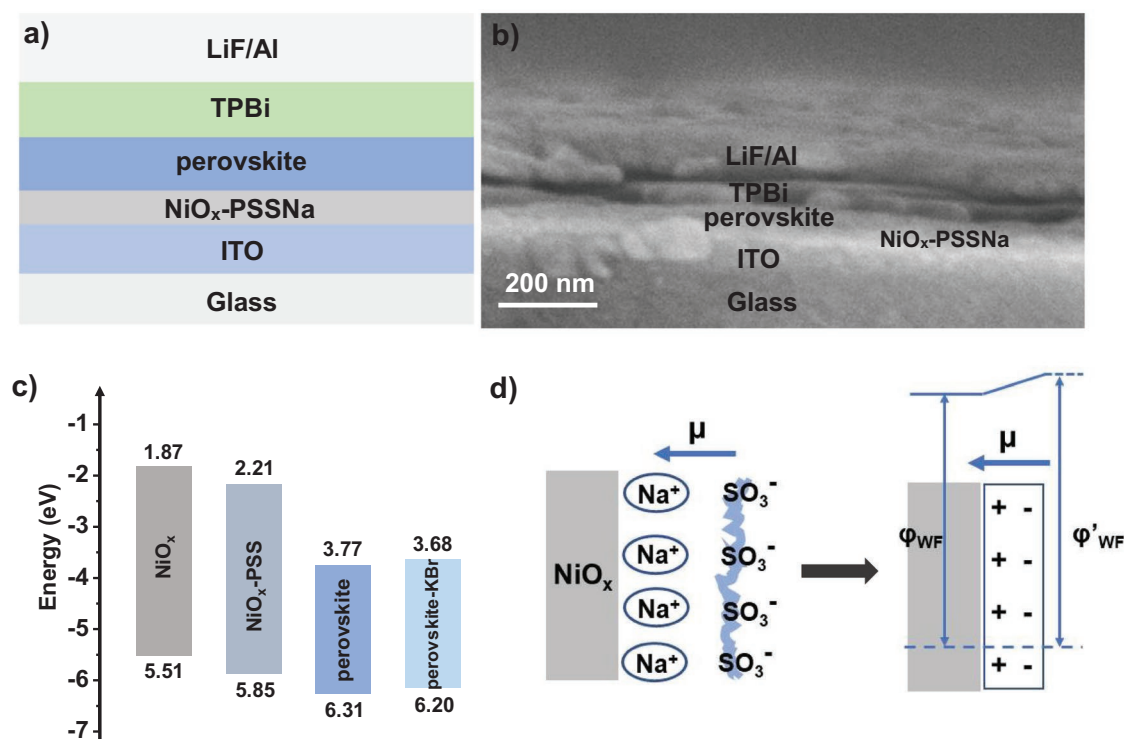


Figure 3. a) Schematic illustration of the blue PeLED with structure of glass/ITO/ NiO_x -PSSNa/perovskite/TPBi/LiF/Al, b) cross-sectional SEM image of the PeLEDs, c) energy levels for NiO_x , NiO_x -PSSNa, quasi-2D perovskite, and quasi-2D perovskite decorated with KBr, and d) dipole moment formation on NiO_x by PSSNa and the increased work function of NiO_x -PSSNa film by the dipole moment.

PSSNa layer. Figure 3d illustrates the shift of vacuum energy level at NiO_x -PSSNa surface due to the dipole moment. With the dipole moment pointing toward NiO_x surface, the vacuum energy level at NiO_x -PSSNa surface can be increased, which results in the increased work function of NiO_x -PSSNa film. The lower energy level of NiO_x -PSSNa bilayer structure will reduce the energy barrier for hole injection and lower the turn-on voltage of PeLEDs as described later. In addition, the KBr decoration will slightly lift up the energy band of the perovskite (see Figure 3c) which further narrow down the energy barrier for efficient carrier injection.

The EL spectra of PeLEDs are shown in Figure 4a, where the emission peaks are at 487 nm for the quasi-2D PeLEDs with NiO_x only and NiO_x -PSSNa as the hole transport layer, and the peak is centered at 492 nm for NiO_x -PSSNa-KBr PeLEDs (i.e., the KBr decorated quasi-2D PeLEDs with NiO_x -PSSNa bilayer as the hole transport layer), in which all of them display neglectable blueshifts compared with their PL peaks indicating that light emission is solely from the quasi-2D perovskite layers. In other words, there is a good confinement of both injected electrons and holes within the quasi-2D perovskite emission layer in all these PeLEDs. From the current density–voltage characteristics, there is a relatively higher leakage current for NiO_x -only PeLEDs (Figure 4b), which is ascribed to the poor film morphology and mass trap states at interfaces. After tailoring the interfacial contact with PSSNa, the injection current was significantly reduced indicating the leakage current has been inhibited. The turn-on (threshold) voltage (V_{th} , corresponding with luminance of 1 cd m^{-2}) of NiO_x -only PeLEDs

is 3.77 V. The V_{th} was further decreased from 3.77 V for NiO_x device to 3.36 and 3.31 V for NiO_x -PSSNa and NiO_x -PSSNa-KBr devices, respectively (Figure 4c), due to the decreased injection barrier favoring us to achieve one of the lowest turn-on voltage as compared to the reported blue PeLEDs.^[34,39,63]

The NiO_x -only PeLEDs show a maximum brightness (L_{max}) of 1199 cd m^{-2} at bias of 7.2 V, which has been increased to 1748 cd m^{-2} for NiO_x -PSSNa bilayered device at the same bias (Table 1). Consistent with the trend, the enhancements are also observed in quantum efficiency and current efficiency (CE), with EQE increasing from 0.36 to 0.78% (Figure 4d), and CE reaching from 0.44 to 1.03 cd A^{-1} (Figure 4e), respectively. These improvements indicate the process of nonradiative recombination has been effectively suppressed by PSSNa insertion. To further reveal the role of PSSNa, the PeLED performances, different concentrations of PSSNa solution treatments were investigated as shown in Figure S13 (Supporting Information). It can be observed that too thick PSSNa layer will harm the device performance owing to the induced low hole injection rate (Figure S14, Supporting Information). By introducing NiO_x -PSSNa-KBr PeLEDs, the device performances were further improved. The CE and EQE are improved to 2.25 cd A^{-1} and 1.45%, respectively. Remarkably, a high L_{max} of 4359 cd m^{-2} is also achieved, which is further improved to 5737 cd m^{-2} by optimizing the perovskite precursor concentration (Figure 4f, and Figure S15, Supporting Information). To the best of our knowledge, this is the brightest blue perovskite-based LEDs reported to date (Table S3, Supporting Information). In addition, the devices also exhibited good reproducibility with average

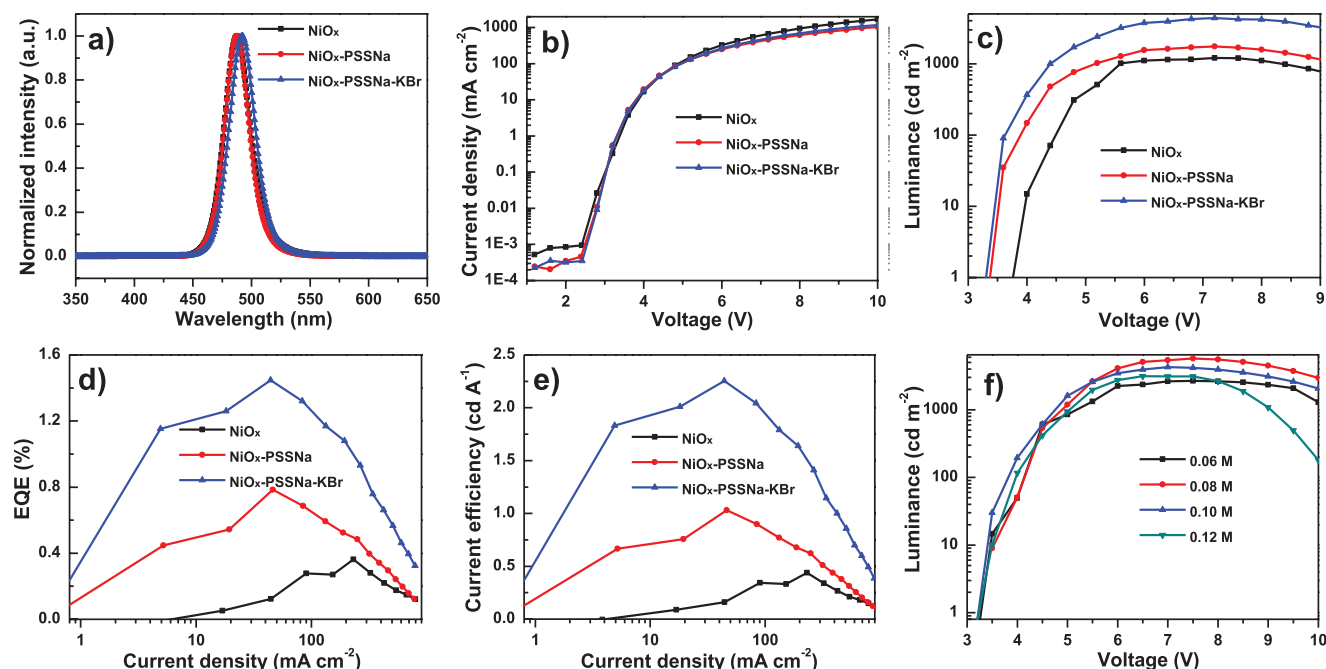


Figure 4. a) EL spectra of NiO_x , $\text{NiO}_x\text{-PSSNa}$, and $\text{NiO}_x\text{-PSSNa-KBr}$ blue PeLEDs, and the corresponding b) current density–voltage (J – V) characteristics, c) luminance–voltage (L – V), d) EQE, e) current efficiency curves, and f) L – V curve of $\text{NiO}_x\text{-PSSNa-KBr}$ blue PeLEDs with different perovskite precursor concentrations.

EQE of 1.26% and luminance of 3794 cd m^{-2} (Figure S16, Supporting Information). This improvement is mainly due to the passivation of defects in perovskite films. The effects of KBr concentration on the device performance are optimized as shown Figure S17 (Supporting Information). The device with 10% KBr shows the highest L_{max} and EQE, and the performance begins to decline with further increase of the concentration. It is because the too high potassium concentration will reduce the carrier injection rate for the device (Figure S18, Supporting Information). Besides, a seriously decreased PLQY is observed from 18.7% (10% KBr) to 7.2% (20% KBr) (Figure S19, Supporting Information) resulting from the impurity phase (Figure S20, Supporting Information). Differently, at low potassium concentration (10% KBr) without any heating treatment, there is no additional impurity phase nor obvious peak shift (Figure S20c, Supporting Information) in the XRD spectra of the perovskite film, which indicates that the potassium cations dominantly distributed at the perovskite film surface and boundaries,^[55–57] as further demonstrated by the conductive AFM measurements (Figure S21, Supporting Information) where the conductivity of perovskite grain boundaries and surfaces increases with decoration of potassium cations. However, increasing the potassium concentration and implementing the

heating treatment will both promote the formation of the impurity phases which cause a serious decrease of the emitting properties of the decorated perovskite films (Figures S19 and S20, Supporting Information).

The spectral stability of $\text{NiO}_x\text{-PSSNa-KBr}$ PeLEDs against the bias current has been studied as shown in Figure 5a. The intensity of the peaks increases at first with increasing the voltage (from 5 V ($1613.54 \text{ cd m}^{-2}$, $106.91 \text{ mA cm}^{-2}$) to 7 V ($4329.43 \text{ cd m}^{-2}$, $465.23 \text{ mA cm}^{-2}$)). It will decline at higher bias voltages of 8 V ($4155.96 \text{ cd m}^{-2}$, $694.77 \text{ mA cm}^{-2}$) to 10 V ($2014.35 \text{ cd m}^{-2}$, $1182.92 \text{ mA cm}^{-2}$). Interestingly, the position of the emission peaks remains at 492 nm with a full width at half maximum (FWHM) of $\approx 26 \text{ nm}$. The EL image of the device under operation is in the inset of Figure 5b and the Commission Internationale de L'Eclairage (CIE) chromaticity coordinates is (0.065, 0.384), and the CIE chromaticity coordinates for NiO_x and $\text{NiO}_x\text{-PSSNa}$ devices are shown in Figure S22 (Supporting Information). Regarding lifetime of the PeLEDs, the time-dependent stability of the device is plotted in Figure 5c. It can be seen that the PeLED with a lower initial luminance tends to show longer operating lifetime, as the lifetimes are 220 and 120 min corresponding to the initial luminance of 150 and 415 cd m^{-2} , respectively. The performance of the devices under continuous constant current was also measured (Figure S23, Supporting Information), the $\text{NiO}_x\text{-PSSNa-KBr}$ device shows much longer lifetime than NiO_x and $\text{NiO}_x\text{-PSSNa}$ devices. It is also noted that the spectra of the devices are stable without any shift of the peaks during the lifetime measurements (Figure S24, Supporting Information) indicating a promising prospect of our quasi-2D perovskites for PeLEDs. Consequently, the blue $\text{NiO}_x\text{-PSSNa-KBr}$ quasi-2D PeLED shows very stable color characteristics at a wide range of driving current

Table 1. Device performance of NiO_x , $\text{NiO}_x\text{-PSSNa}$, and $\text{NiO}_x\text{-PSSNa-KBr}$ PeLEDs.

Devices	V_{th} [V]	L_{max} [cd m^{-2}]	CE [cd A^{-1}]	EQE [%]
NiO_x	3.77	1199	0.44	0.36
$\text{NiO}_x\text{-PSSNa}$	3.36	1748	1.03	0.78
$\text{NiO}_x\text{-PSSNa-KBr}$	3.31	4359	2.25	1.45

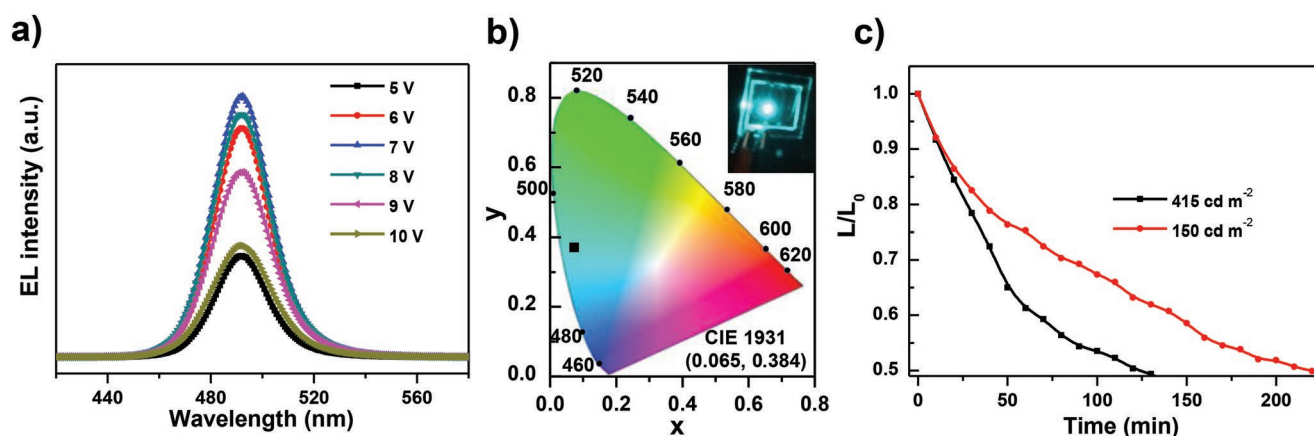


Figure 5. EL properties of NiO_x -PSSNa-KBr PeLEDs. a) EL spectra of NiO_x -PSSNa-KBr PeLEDs at different biased voltages, and b) the corresponding CIE coordinate (the emission image is shown in the inset). c) The lifetime of the blue PeLEDs with different initial luminance tested every 10 min at a constant current with a blink way.

density from 106.91 to 1182.92 mA cm^{-2} which is very important for practical applications. In addition, the NiO_x -PSSNa-KBr PeLEDs show very good spectral stability and much longer operation lifetime than the previous reports.^[39]

3. Conclusion

In conclusion, we report an effective hole transport bilayer structure by introducing a thin layer of PSSNa on NiO_x for highly performed blue quasi-2D PeLEDs. The introduction of PSSNa can simultaneously reduce defect states at NiO_x surface and improve the morphology (through minimizing pinholes and surface roughness) of perovskite films. These two advantages contribute to inhibit the mass nonradiative recombination. Besides, the low valance band of NiO_x -PSSNa films minimizes the energy barrier for efficient hole injection. Meanwhile, with the KBr decoration in the quasi-2D perovskite ($\text{PA}_2(\text{CsPbBr}_3)_{n-1}\text{PbBr}_4$), the nonradiative losses are further suppressed by passivating the traps within perovskite films. The blue NiO_x -PSSNa-KBr based PeLEDs show very low turn-on voltage of 3.31 V, and an EQE of 1.45% with an impressive luminance of 4359 cd m^{-2} , which is further improved to 5737 cd m^{-2} by optimizing the perovskite precursor concentration. This is above 1.5-fold higher than that of the best reported blue PeLED and represents the brightest blue PeLED so far from our best knowledge. In addition, the devices also show good spectral stability and operation lifetime as compared to other blue PeLEDs. The results signal a great potential of blue PeLEDs toward the practical applications.

4. Experimental Section

NiO_x Nanoparticles Synthesis: The NiO_x nanoparticles were fabricated through the chemical precipitation method with certain modifications.^[54] Typically, 10 mmol nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was dissolved in 60 mL deionized water and stirred for 5 min to get a dark green solution. Then the pH of this solution was adjusted to 10 by dropping the 0.5 M NaOH solution. After stirring for several minutes, the green precipitation was centrifuged to separate from the solution, and washed several times with deionized water and ethanol. The

precipitation was dried at 70 °C for 12 h, and then transferred into muffle furnace, calcined at 270 °C for 2 h to get a black powder. Then the desired concentration of NiO_x solution was obtained by directly dissolving the powder into deionized water.

Preparation of the Quasi-2D Perovskite: CsPbBr_3 powder was first synthesized, specifically, 5 mmol PbBr_2 was dissolved in hydrobromic acid and stirring for 10 min, then 1.5 mL CsBr aqueous solution (3.4 M) was dropped to get an orange solution. The precipitation was centrifuged from the solution, and thoroughly washed with diethyl ether and ethanol for several times, then dried at 60 °C for 12 h to obtain an orange powder. The quasi-2D perovskite was prepared by first dissolving 0.1 M CsPbBr_3 powder and 0.1 M propylamine hydrobromide (PABr) into DMSO, then spin-coated at 3000 rpm for 60 s and 200 μL of toluene was dropped on the rotating substrate at 30 s after the spin-procedure starting. For KBr decorated perovskite, the preparation process is similar to that of quasi-2D perovskite except for different concentrations ($n = n_{\text{KBr}}/(n_{\text{CsPbBr}_3} + n_{\text{PABr}})$) of KBr were added into the precursor.

Device Fabrication: ITO substrates were successively cleaned with deionized water, acetone, and isopropyl alcohol solvents, and finally treated with ultraviolet-ozone for 20 min to remove any residues left on the substrates. Then the NiO_x solution with concentration of 20 mg mL^{-1} was spin-coated on ITO substrates at 2000 rpm for 60 s. The NiO_x -PSSNa films were obtained by spin-coating different concentrations of PSSNa methanol solution (0.025, 0.05, and 0.10 wt%) on NiO_x films at 3000 rpm for 45 s. Then the perovskite precursor solution was spin-coated on the substrates without need of heating. It is noted that the concentrations for PSSNa and KBr used in the text are 0.025 wt% and 10%, respectively. After completion of perovskite films, 50 nm TPBi, 1 nm LiF and 100 nm Al electrode were thermally evaporated onto the perovskite films with deposition rates of 0.5, 0.03, and 1 $\text{\AA s}^{-1}$, respectively, to complete the device fabrication, and then sealed by an ultraviolet-curable resin and stored in the dryer for 1 d before testing. For the hole-only devices, the perovskite films were prepared on the hole transport layer (NiO_x or NiO_x -PSSNa film). Then 45 nm 4,4'-bis(N-carbazolyl)-1,1'-biphenyl (CBP), 10 nm MoO_3 , and 100 nm Al electrode were thermally evaporated onto the perovskite films with deposition rates of 0.5, 0.2, and 1 $\text{\AA s}^{-1}$, respectively, to complete the device fabrications.

Characterization: UV-vis absorption spectra were recorded on a PERSEE TU-1901 spectrophotometer. The morphology of perovskite thin films and the cross-sectional SEM images were characterized by scanning electron microscope (Zeiss 1550). X-ray diffraction analysis was carried out with X-ray diffractometer (Bruker Advance D8 Ew Germany) with $\text{Cu K}\alpha$ radiation. AFM images were measured by the atomic force microscope of NanoScope III (Digital Instrument). The UPS analysis was carried out using a KRATOS ULTRA AXIS DLD photoelectron

spectroscopy system with an unfiltered He I (21.22 eV) gas-discharge lamp. The PLQY were carried out with an equipment of Hamamatsu Quantaurus-QY, model no. C11347. The steady-state and time-resolved photoluminescence of perovskite on glass were investigated using PicoQuant FluoTime 300 equipped with a picosecond pulse laser (375 nm, LDH-P-C-375) with a pulse width of <40 ps. The perovskite films were excited by a repetition rate of 2 MHz. The time-resolved single was measured by a time-corrected single photon counting (TCSPC, PicoHarp 300E) module with photomultiplier (PMA-C 192-M) detector. The current density–voltage–luminance curves were acquired using an Ocean Optics system equipped with a Keithley 2450 source meter and an integrating sphere which was connected to an Ocean Optics QE65000 spectrometer. The integrating sphere was calibrated with a radiometric calibration light source before use. The CIE coordinate of the device was calculated using software LED Color Calculator (OSRAM). In the text, the time-dependent lifetime measurements of devices were tested in every 10 min, the devices were lighted up by a blink way with the lighting time of 3 s by a constant current for each test. Furthermore, the operation lifetime of the devices under a continuous constant current (the devices are lighted up all the time during the test) was also measured as shown in the Supporting Information.

Supporting Information

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

Acknowledgements

This research was supported by Equipment fund, Platform Research Fund and feed fund (Grant Nos. 201611159194, 201511159225, and 201811159147), from the University Grant Council of the University of Hong Kong as well as the General Research Fund (Grant Nos. 17211916, 17204117, and 17200518) from Hong Kong Special Administrative Region, China. The authors acknowledge Prof. Rui Chen, Jiahao Yu, Jiayun Sun, Shihao Ding, and Zhaojin Wang for their help in characterization.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

blue perovskite LEDs, carrier transport layer, high luminance, quasi-2D perovskite, turn-on voltage

Received: July 3, 2019

Published online:

- [1] H. S. Kim, C. R. Lee, J. H. Im, K. B. Lee, T. Moehl, A. Marchioro, S. J. Moon, R. Humphry-Baker, J. H. Yum, J. E. Moser, M. Gratzel, N. G. Park, *Sci. Rep.* **2012**, *2*, 591.
- [2] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, *J. Am. Chem. Soc.* **2009**, *131*, 6050.
- [3] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, H. J. Snaith, *Science* **2012**, *338*, 643.
- [4] L. Dou, Y. M. Yang, J. You, Z. Hong, W.-H. Chang, G. Li, Y. Yang, *Nat. Commun.* **2014**, *5*, 5404.
- [5] Y. Fang, J. Huang, *Adv. Mater.* **2015**, *27*, 2804.

- [6] J. Luo, X. Wang, S. Li, J. Liu, Y. Guo, G. Niu, L. Yao, Y. Fu, L. Gao, Q. Dong, C. Zhao, M. Leng, F. Ma, W. Liang, L. Wang, S. Jin, J. Han, L. Zhang, J. Etheridge, J. Wang, Y. Yan, E. H. Sargent, J. Tang, *Nature* **2018**, *563*, 541.
- [7] Z.-K. Tan, R. S. Moghaddam, M. L. Lai, P. Docampo, R. Higler, F. Deschler, M. Price, A. Sadhanala, L. M. Pazos, D. Credgington, F. Hanusch, T. Bein, H. J. Snaith, R. H. Friend, *Nat. Nanotechnol.* **2014**, *9*, 687.
- [8] J. Song, J. Li, X. Li, L. Xu, Y. Dong, H. Zeng, *Adv. Mater.* **2015**, *27*, 7162.
- [9] S. Yuan, Z.-K. Wang, M.-P. Zhuo, Q.-S. Tian, Y. Jin, L.-S. Liao, *ACS Nano* **2018**, *12*, 9541.
- [10] L. N. Quan, F. Pelayo García de Arquer, R. P. Sabatini, E. H. Sargent, *Adv. Mater.* **2018**, *30*, 1801996.
- [11] M. Yuan, L. N. Quan, R. Comin, G. Walters, R. Sabatini, O. Voznyy, S. Hoogland, Y. Zhao, E. M. Beauregard, P. Kanjanaboos, Z. Lu, D. H. Kim, E. H. Sargent, *Nat. Nanotechnol.* **2016**, *11*, 872.
- [12] K. Lin, J. Xing, L. N. Quan, F. Pelayo García de Arquer, X. Gong, J. Lu, L. Xie, W. Zhao, D. Zhang, C. Yan, W. Li, X. Liu, Y. Lu, J. Kirman, E. H. Sargent, Q. Xiong, Z. Wei, *Nature* **2018**, *562*, 245.
- [13] Y. Cao, N. Wang, H. Tian, J. Guo, Y. Wei, H. Chen, Y. Miao, W. Zou, K. Pan, Y. He, H. Cao, Y. Ke, M. Xu, Y. Wang, M. Yang, K. Du, Z. Fu, D. Kong, D. Dai, Y. Jin, G. Li, H. Li, Q. Peng, J. Wang, W. Huang, *Nature* **2018**, *562*, 249.
- [14] J. Song, T. Fang, J. Li, L. Xu, F. Zhang, B. Han, Q. Shan, H. Zeng, *Adv. Mater.* **2018**, *30*, 1805409.
- [15] M. Ban, Y. Zou, J. P. H. Rivett, Y. Yang, T. H. Thomas, Y. Tan, T. Song, X. Gao, D. Credington, F. Deschler, H. Sirringhaus, B. Sun, *Nat. Commun.* **2018**, *9*, 3892.
- [16] L. Zhang, X. Yang, Q. Jiang, P. Wang, Z. Yin, X. Zhang, H. Tan, Y. M. Yang, M. Wei, B. R. Sutherland, E. H. Sargent, J. You, *Nat. Commun.* **2017**, *8*, 15640.
- [17] T. Chiba, Y. Hayashi, H. Ebe, K. Hoshi, J. Sato, S. Sato, Y.-J. Pu, S. Ohisa, J. Kido, *Nat. Photonics* **2018**, *12*, 681.
- [18] J. Pan, Y. Shang, J. Yin, M. De Bastiani, W. Peng, I. Dursun, L. Sinatra, A. M. El-Zohry, M. N. Hedhili, A.-H. Emwas, O. F. Mohammed, Z. Ning, O. M. Bakr, *J. Am. Chem. Soc.* **2018**, *140*, 562.
- [19] S. Zhang, C. Yi, N. Wang, Y. Sun, W. Zou, Y. Wei, Y. Cao, Y. Miao, R. Li, Y. Yin, N. Zhao, J. Wang, W. Huang, *Adv. Mater.* **2017**, *29*, 1606600.
- [20] Z. Xiao, R. A. Kerner, L. Zhao, N. L. Tran, K. Lee, T.-W. Koh, G. D. Scholes, B. P. Rand, *Nat. Photonics* **2017**, *11*, 108.
- [21] Z. Wang, Q. Lin, F. P. Chmiel, N. Sakai, L. M. Herz, H. J. Snaith, *Nat. Energy* **2017**, *2*, 17135.
- [22] H. Wang, X. Zhang, Q. Wu, F. Cao, D. Yang, Y. Shang, Z. Ning, W. Zhang, W. Zheng, Y. Yan, S. V. Kershaw, L. Zhang, A. L. Rogach, X. Yang, *Nat. Commun.* **2019**, *10*, 665.
- [23] L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh, M. V. Kovalenko, *Nano Lett.* **2015**, *15*, 3692.
- [24] E.-P. Yao, Z. Yang, L. Meng, P. Sun, S. Dong, Y. Yang, Y. Yang, *Adv. Mater.* **2017**, *29*, 1606859.
- [25] A. Sadhanala, S. Ahmad, B. Zhao, N. Giesbrecht, P. M. Pearce, F. Deschler, R. L. Z. Hoye, K. C. Gödel, T. Bein, P. Docampo, S. E. Dutton, M. F. L. De Volder, R. H. Friend, *Nano Lett.* **2015**, *15*, 6095.
- [26] S. Draguta, O. Sharia, S. J. Yoon, M. C. Brennan, Y. V. Morozov, J. S. Manser, P. V. Kamat, W. F. Schneider, M. Kuno, *Nat. Commun.* **2017**, *8*, 200.
- [27] Y. Wu, C. Wei, X. Li, Y. Li, S. Qiu, W. Shen, B. Cai, Z. Sun, D. Yang, Z. Deng, H. Zeng, *ACS Energy Lett.* **2018**, *3*, 2030.
- [28] Y. Chen, Y. Sun, J. Peng, J. Tang, K. Zheng, Z. Liang, *Adv. Mater.* **2018**, *30*, 1703487.
- [29] Y. Zhang, J. Liu, Z. Wang, Y. Xue, Q. Ou, L. Polavarapu, J. Zheng, X. Qi, Q. Bao, *Chem. Commun.* **2016**, *52*, 13637.

- [30] D. Liang, Y. Peng, Y. Fu, M. J. Shearer, J. Zhang, J. Zhai, Y. Zhang, R. J. Hamers, T. L. Andrew, S. Jin, *ACS Nano* **2016**, *10*, 6897.
- [31] X. Yang, X. Zhang, J. Deng, Z. Chu, Q. Jiang, J. Meng, P. Wang, L. Zhang, Z. Yin, J. You, *Nat. Commun.* **2018**, *9*, 570.
- [32] J. Byun, H. Cho, C. Wolf, M. Jang, A. Sadhanala, R. H. Friend, H. Yang, T.-W. Lee, *Adv. Mater.* **2016**, *28*, 7515.
- [33] H.-D. Lee, H. Kim, H. Cho, W. Cha, Y. Hong, Y.-H. Kim, A. Sadhanala, V. Venugopalan, J. S. Kim, J. W. Choi, C.-L. Lee, D. Kim, H. Yang, R. H. Friend, T.-W. Lee, *Adv. Funct. Mater.* **2019**, 1901225.
- [34] Z. Chen, C. Zhang, X.-F. Jiang, M. Liu, R. Xia, T. Shi, D. Chen, Q. Xue, Y.-J. Zhao, S. Su, H.-L. Yip, Y. Cao, *Adv. Mater.* **2017**, *29*, 1603157.
- [35] L. Cheng, Y. Cao, R. Ge, Y.-Q. Wei, N.-N. Wang, J.-P. Wang, W. Huang, *Chin. Chem. Lett.* **2017**, *28*, 29.
- [36] D. N. Congreve, M. C. Weidman, M. Seitz, W. Paritmongkol, N. S. Dahod, W. A. Tisdale, *ACS Photonics* **2017**, *4*, 476.
- [37] P. Vashishtha, M. Ng, S. B. Shivarudraiah, J. E. Halpert, *Chem. Mater.* **2019**, *31*, 83.
- [38] Q. Wang, J. Ren, X.-F. Peng, X.-X. Ji, X.-H. Yang, *ACS Appl. Mater. Interfaces* **2017**, *9*, 29901.
- [39] J. Xing, Y. Zhao, M. Askerka, L. N. Quan, X. Gong, W. Zhao, J. Zhao, H. Tan, G. Long, L. Gao, Z. Yang, O. Voznyy, J. Tang, Z.-H. Lu, Q. Xiong, E. H. Sargent, *Nat. Commun.* **2018**, *9*, 3541.
- [40] Z. Li, Z. Chen, Y. Yang, Q. Xue, H.-L. Yip, Y. Cao, *Nat. Commun.* **2019**, *10*, 1027.
- [41] S. Hou, M. K. Gangishetty, Q. Quan, D. N. Congreve, *Joule* **2018**, *2*, 2421.
- [42] Y. Zou, M. Ban, Y. Yang, S. Bai, C. Wu, Y. Han, T. Wu, Y. Tan, Q. Huang, X. Gao, T. Song, Q. Zhang, B. Sun, *ACS Appl. Mater. Interfaces* **2018**, *10*, 24320.
- [43] X. Zhang, C. Sun, Y. Zhang, H. Wu, C. Ji, Y. Chuai, P. Wang, S. Wen, C. Zhang, W. W. Yu, *J. Phys. Chem. Lett.* **2016**, *7*, 4602.
- [44] X. Zhang, H. Lin, H. Huang, C. Reckmeier, Y. Zhang, W. C. H. Choy, A. L. Rogach, *Nano Lett.* **2016**, *16*, 1415.
- [45] Y.-H. Kim, C. Wolf, Y.-T. Kim, H. Cho, W. Kwon, S. Do, A. Sadhanala, C. G. Park, S.-W. Rhee, S. H. Im, R. H. Friend, T.-W. Lee, *ACS Nano* **2017**, *11*, 6586.
- [46] K.-C. Wang, J.-Y. Jeng, P.-S. Shen, Y.-C. Chang, E. W.-G. Diau, C.-H. Tsai, T.-Y. Chao, H.-C. Hsu, P.-Y. Lin, P. Chen, T.-F. Guo, T.-C. Wen, *Sci. Rep.* **2015**, *4*, 4756.
- [47] J.-Y. Jeng, K.-C. Chen, T.-Y. Chiang, P.-Y. Lin, T.-D. Tsai, Y.-C. Chang, T.-F. Guo, P. Chen, T.-C. Wen, Y.-J. Hsu, *Adv. Mater.* **2014**, *26*, 4107.
- [48] Z. H. Bakr, Q. Wali, A. Fakharuddin, L. Schmidt-Mende, T. M. Brown, R. Jose, *Nano Energy* **2017**, *34*, 271.
- [49] W. Chen, Y. Zhou, L. Wang, Y. Wu, B. Tu, B. Yu, F. Liu, H.-W. Tam, G. Wang, A. B. Djuricic, L. Huang, Z. He, *Adv. Mater.* **2018**, *30*, 1800515.
- [50] Z. Zhu, Y. Bai, T. Zhang, Z. Liu, X. Long, Z. Wei, Z. Wang, L. Zhang, J. Wang, F. Yan, S. Yang, *Angew. Chem., Int. Ed. Engl.* **2014**, *53*, 12571.
- [51] M. K. Gangishetty, S. Hou, Q. Quan, D. N. Congreve, *Adv. Mater.* **2018**, *30*, 1706226.
- [52] K.-H. Wang, Y. Peng, J. Ge, S. Jiang, B.-S. Zhu, J.-S. Yao, Y.-C. Yin, J.-N. Yang, Q. Zhang, H.-B. Yao, *ACS Photonics* **2019**, *6*, 667.
- [53] Z. Li, C. Xiao, Y. Yang, S. P. Harvey, D. H. Kim, J. A. Christians, M. Yang, P. Schulz, S. U. Nanayakkara, C.-S. Jiang, J. M. Luther, J. J. Berry, M. C. Beard, M. M. Al-Jassima, K. Zhu, *Energy Environ. Sci.* **2017**, *10*, 1234.
- [54] F. Jiang, W. C. H. Choy, X. Li, D. Zhang, J. Cheng, *Adv. Mater.* **2015**, *27*, 2930.
- [55] W. Zhao, Z. Yao, F. Yu, D. Yang, S. Liu, *Adv. Sci.* **2018**, *5*, 1700131.
- [56] M. Abdi-Jalebi, Z. Andaji-Garmaroudi, S. Cacovich, C. Stavarakas, B. Philippe, J. M. Richter, M. Alsari, E. P. Booker, E. M. Hutter, A. J. Pearson, S. Lilliu, T. J. Savenije, H. Rensmo, G. Divitini, C. Ducati, R. H. Friend, S. D. Stranks, *Nature* **2018**, *555*, 497.
- [57] J. Cao, S. X. Tao, P. A. Bobbert, C.-P. Wong, N. Zhao, *Adv. Mater.* **2018**, *30*, 1707350.
- [58] C. Wu, T. Wu, Y. Yang, J. A. McLeod, Y. Wang, Y. Zou, T. Zhai, J. Li, M. Ban, T. Song, X. Gao, S. Duhm, H. Sirringhaus, B. Sun, *ACS Nano* **2019**, *13*, 1645.
- [59] M. Kumagai, T. Takagahara, *Phys. Rev. B* **1989**, *40*, 12359.
- [60] J.-C. Blancon, H. Tsai, W. Nie, C. C. Stoumpos, L. Pedesseau, C. Katan, M. Kepenekian, C. M. M. Soe, K. Appavoo, M. Y. Sfeir, S. Tretiak, P. M. Ajayan, M. G. Kanatzidis, J. Even, J. J. Crochet, A. D. Mohite, *Science* **2017**, *355*, 1288.
- [61] H. Cho, S.-H. Jeong, M.-H. Park, Y.-H. Kim, C. Wolf, C.-L. Lee, J. H. Heo, A. Sadhanala, N. Myoung, S. Yoo, S. H. Im, R. H. Friend, T.-W. Lee, *Science* **2015**, *350*, 1222.
- [62] D. Shi, V. Adinolfi, R. Comin, M. Yuan, E. Alarousu, A. Buin, Y. Chen, S. Hoogland, A. Rothenberger, K. Katsiev, Y. Losovyj, X. Zhang, P. A. Dowben, O. F. Mohammed, E. H. Sargent, O. M. Bakr, *Science* **2015**, *347*, 519.
- [63] S. Kumar, J. Jagielski, S. Yakunin, P. Rice, Y.-C. Chiu, M. Wang, G. Nedelcu, Y. Kim, S. Lin, E. J. G. Santos, M. V. Kovalenko, C.-J. Shih, *ACS Nano* **2016**, *10*, 9720.