Rapid Crystallization of All-Inorganic CsPbBr₃ Perovskite for High-Brightness Light-Emitting Diodes

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ABSTRACT: Research into perovskite-based light-emitting diodes (PeLEDs) has been rapidly gaining momentum since the initial reports of green-emitting methylammonium lead bromide (CH₃NH₃PbBr₃)-based devices were published. However, issues pertaining to its stability and morphological control still hamper progress toward high performing devices. Solvent engineering, a technique typically employed to modulate film crystallization, offers little opportunity for scale-up due to the tendency for inhomogeneous film growth and low degree of reproducibility. Here, we propose and show a simple gas-facilitated process to deposit a stable, all-inorganic perovskite CsPbBr₃ film. The formation of smaller and less percolated grains, which gives rise to enhanced optical properties, highlights the importance of spatial charge confinement in the film. Consequently, the performance of our PeLEDs shows great improvement, with luminance as high as 8218 cd m⁻² and turn-on voltage as low as 2.4 V. Concomitantly, the current efficiency and EQE of our device were increased to 0.72 cd A⁻¹ and 0.088%, respectively. High reproducibility in the performance of PeLEDs fabricated using this process opens the path for large-area devices.

INTRODUCTION

Perovskites have gained much attention from the scientific community in the last decade, creating waves particularly in the field of photovoltaics. Although traditionally used to classify materials adopting a structure similar to that of calcium titanate,¹ in recent research in the field of solar energy, this term refers specifically to a compound comprising an organic—inorganic hybrid cation (CH₃NH₃⁺), a divalent metal (Pb²⁺), and a monovalent halide anion (I⁻), arranged in a three-dimensional network of corner-sharing PbI₆ octahedra surrounding the central CH₃NH₃ cation. The unprecedented expeditious rise in power conversion efficiencies for perovskite-based solar cells, from a mere 3.8%² to an excess of 20%³,⁴ puts it in the same stead as the best in class thin-film CIGS and CdTe solar cells to date.⁵ It is thus unsurprising that this new generation of photovoltaics has managed to claim a spot in the list of Science’s Top 10 Breakthroughs in 2013.⁶ The versatility and excellent optoelectronic properties exhibited by this principal material, such as balanced long-range charge trans-
Figure 1. (a) Schematic illustration of the N₂-facilitated film formation during the spin-coating process. (b) XRD spectra (* corresponds to ITO peaks), (c) absorption and photoluminescence (PL) spectra, and (d) time-resolved photoluminescence (TRPL) decay curves (solid lines are fitted curves) of conventional (black) and N₂-facilitated (red) CsPbBr₃ films.

(such as by tailoring the interfacial charge transport layers, employing a polymer-perovskite blend, and using solvent engineering techniques to enhance film formation) have given rise to improvements in current efficiency of up to 42.9 cd A⁻¹ and in external quantum efficiency (EQE) of up to 8.53%. Despite its outstanding potential, long-term stability has been one of the major concerns hindering its widespread use. Moisture exposure can induce degradation of the material due to the affinity of organic cations to water molecules. Moreover, its thermal stability is also governed by the low-temperature sublimation of the organic cations. Fully inorganic perovskite materials have been reported by substituting the organic cation with Cs⁺, giving the materials higher resistance to thermal degradation. However, research into these materials has been minimal as compared to that of their organic-inorganic counterparts. The first CsPbBr₃ PeLED paper reported a reduced trap density with excess CsBr in the precursor solution, where the material achieved an $I_{\text{max}}$ of 407 cd m⁻² and a current efficiency level of 0.035 cd A⁻¹. The passivation of atomic Pb defects with the excess CsBr was key to reducing nonradiative decay pathways, as supported by Cho’s group. Zhang et al. also demonstrated PeLEDs employing CsPbBr₃ nanocrystals, which achieved an improved $I_{\text{max}}$ and current efficiency of 1377 cd m⁻² and 0.19 cd A⁻¹, respectively, through interface engineering. Recently, a new synthetic approach of PEO-assisted CsPbBr₃ films has been demonstrated, yielding a smoother and pinhole-free morphology with smaller crystals, leading to highly luminescent and efficient PeLEDs.

In both organic-inorganic hybrid (CH₃NH₃PbBr₃) and fully inorganic (CsPbBr₃) systems, a smaller grain size and thus increased grain boundary area are expected to be beneficial for PeLEDs due to the spatial confinement of excitons and charge carriers within the restricted nanoscale geometries that consequently blocks their diffusion and thereby increases radiative recombination. This has been demonstrated in several reports where processing has been modified in various ways to modulate grain size, such as through nanocrystal pinning, a quick annealing process, and incorporation in a polymer matrix. Morphology has therefore been reaffirmed to be a critical factor in determining the performance of the final devices and this can be tuned via engineering the deposition and formation of the perovskite thin film.

Film formation plays a pivotal role in determining the morphology, which in turn is responsible for the resultant properties of the perovskite film, especially the charge carrier dynamics. A major factor influencing this is the crystallization rate. Padture et al. reported a comprehensive study to understand solution-processed perovskite film formation, with a particular emphasis on the nucleation, growth, coarsening, and evolution aspects. The slow evaporation of commonly used solvents (e.g., dimethylformamide and dimethyl sulfoxide (DMSO)) due to their high boiling points somewhat hindered the perovskite crystallization during the spin-coating process. As a result, low nuclei density led to acicular structures and incomplete coverage from the conventional spin-coating process. A commonly used method to circumvent this problem and achieve highly efficient perovskite solar cells and PeLEDs is to use a solvent engineering method, whereby an antisolvent such as toluene or chloroform is introduced to supersaturate the perovskite precursor solution and induce precipitation. Using this method, the nucleation rate is greatly enhanced and the growth rate is suppressed simultaneously, resulting in a smooth and fine-grained film with good coverage. However, scale-up production of such devices remains hampered by low reproducibility arising from a propensity for a radial and inhomogeneous growth gradient as well as the toxic nature of commonly used antisolvents.

To generate a large nuclei density in a short period of time without the use of antisolvents, an alternative gas-facilitation method is proposed. In this article, we show that by using a simple additional step of nitrogen (N₂) gas flow during the film
formation, we can achieve remarkable improvements in the performance of our PeLED devices. This is possible due to the smaller and less percolated grains formed as a result of the accelerated supersaturation and rapid crystallization facilitated by the introduction of N2 gas, thus allowing for spatial charge confinement and enhanced radiative recombination. By optimizing the pressure and timing of the gas flow, highly luminescent green-emitting PeLEDs based on CsPbBr3 were fabricated with an Lmax exceeding 8000 cd m−2, a turn-on voltage as low as 2.4 V, a current efficiency level in excess of 0.7 cd A−1, and an EQE of over 0.08%.

Table 1. Optical and Photophysical Properties of Conventional and N2-Facilitated CsPbBr3 Films

| sample               | λmax (nm) | FWHM (nm) | PLQY (%) | τPL (ns) | τrad (ns) | τnonrad (ns) |
|----------------------|-----------|-----------|----------|----------|-----------|--------------|
| conventional         | 526       | 17        | 10.9 ± 0.2 | 4.9 ± 0.1 | 45 ± 2    | 5.5 ± 0.2    |
| N2-facilitated       | 524       | 17        | 13.0 ± 0.1 | 3.7 ± 0.1 | 29 ± 1    | 4.3 ± 0.1    |

Figure 2. Surface (top row) and cross-sectional (bottom row) FESEM images of CsPbBr3 films deposited on ITO/PEDOT:PSS substrates using (a, c) conventional and (b, d) N2-facilitated processes.
Recent literature has reported the coexistence of both three-dimensional CsPbBr$_3$ and zero-dimensional Cs$_4$PbBr$_6$ (Bergerhoff–Schmitz–Dumont-type crystal structure) crystals from solution growth. The large difference in solubility between CsBr and PbBr$_2$ in DMSO resulted in the different reactivity of both dissolved species, leading to CsBr-rich Cs$_4$PbBr$_6$ precipitating alongside CsPbBr$_3$. However, the absence of any characteristic XRD peaks in our films verifies that Cs$_4$PbBr$_6$ is not present. The single PL peak for both samples (at 524 and 526 nm) also confirms the absence of Cs$_4$PbBr$_6$, which emits at 520 nm. Because Cs$_4$PbBr$_6$ has a stronger emission at excitation wavelengths of $\lambda > 340$ nm, to substantiate our claim, additional PL measurements were taken at various excitation wavelengths ranging from 300 to 470 nm (Figure S1). Again, no additional PL peak was observed. As Cs$_4$PbBr$_6$ is insoluble in DMSO, it most likely precipitated in the precursor solution. The XRD patterns shown in a previous report confirmed the presence of Cs$_4$PbBr$_6$ in the precipitates. The resultant clear supernatant, which was used for subsequent spin-coating, is thus free of this impurity compound.

To investigate the charge dynamics, photoluminescence quantum yield (PLQY) and TRPL measurements were carried out and the results are summarized in Table 1. The N$_2$-facilitated film shows a slightly higher PLQY of 13% as compared to 11% for the standard film. The TRPL decay spectra (following excitation at 400 nm) for both films are shown in Figure 1d. The PL decay lifetimes were determined by fitting with a single exponential decay function (solid line). The characteristic PL lifetime ($\tau$) extracted is $4.9 \pm 0.1$ ns for the standard film and $3.7 \pm 0.1$ ns for the N$_2$-facilitated film.

Figure 3. (a) Schematic illustration of device architecture, carrier movement, and corresponding energy levels of various layers in the CsPbBr$_3$ PeLEDs used in this work. (b) Electroluminescence spectra of both devices at different driving voltages. Pictures in inset show sample devices under applied bias. (c) Current density and luminance vs driving voltage, (d) current efficiency vs current density, and (e) EQE vs luminance curves of both devices.
Table 2. Comparison of Device Performance of Conventional and N2-Facilitated CsPbBr3 PeLEDs

| sample     | \(L_{\text{max}}\) (cd m\(^{-2}\)) | \(V_{\text{th}}\) (V) | current efficiency (cd A\(^{-1}\)) |
|------------|-------------------------------------|------------------------|-----------------------------------|
|            | best      | average       | best      | average       | best      | average       |
| conventional | 2964      | 2300 ± 900    | 2.6       | 3.2 ± 0.5     | 0.118     | 0.08 ± 0.03   |
| N2-facilitated | 8218      | 7000 ± 1000   | 2.4       | 2.7 ± 0.3     | 0.718     | 0.3 ± 0.2     |

From this, the radiative (\(\tau_{\text{rad}}\)) and nonradiative (\(\tau_{\text{nonrad}}\)) recombination lifetimes can be calculated using \(\tau_{\text{rad}} = \frac{\tau_{\text{PL}}}{\phi}\) and \(\tau_{\text{nonrad}} = \tau_{\text{PL}}/(1 - \phi)\), where \(\phi\) represents PLQY.\(^{46}\) The much shorter radiative lifetime of ~ 29 ns for the N2-facilitated film is ascribed to the smaller and more isolated grains seen from the surface imaging of the film (discussed subsequently), consequently restricting charge movement and triggering faster recombination. The nonradiative lifetime, however, was slightly shorter for the N2-facilitated film (~ 4.3 ns), due to the increased surface area of the isolated grains resulting in additional nonradiative recombination channels.\(^{47,48}\) Hence, the higher PLQY for the film with smaller grain size is a result of the enhanced radiative recombination rate inside the grains, which overwhels the enhanced nonradiative recombination rate at the grain boundaries.

The surface topology and cross-section imaging of the deposited films are shown in Figure 2. Stark dissimilarities in the film morphology using field emission scanning electron microscopy (FESEM) were observed for the two films, where noticeably smaller and less percolated grains were present in the N2-facilitated film. This is attributed to rapid nucleation as a result of the sudden N2 flow, leading to the generation of high nuclei density and suppression of grain growth. However, this also led to a slightly reduced film coverage (Figure 2b). This was further verified using ImageJ, whereby the film prepared via the conventional process showed approximately 80–90% surface coverage whereas the N2-facilitated films showed 65–70% surface coverage. Cross-section imaging indicated a thinner film (85 ± 10 nm) for the N2-facilitated method (Figure 2d) as compared to a thicker film (130 ± 10 nm) via the conventional process (Figure 2c). The thinner and smaller grains more easily confine charges within their geometrical constraints, bringing about a higher probability of radiative recombination, as shown by the shorter radiative lifetime.

**Device Performance.** To investigate the effect of the film morphology on the operation of the CsPbBr3 emitters, complete PeLED devices were fabricated with CsPbBr3 sandwiched between a hole transport material (PEDOT:PSS) and an electron transport material (bathophenanthroline or Bphen). Figure 3a shows the device architecture along with the corresponding energy levels of each layer. The current density and luminance versus driving voltage (\(J–V–L\) data) as well as the current efficiency curves of the devices are presented in Figure 3c,d, respectively. The reproducibility and distribution of the device performance (up to nine devices) can be found in Figure S8. From the \(J–V\) curves (logarithmic plot in Figure S2), the conventional and N2-facilitated devices exhibit an ohmic conduction (\(m = 1\)) of up to 1.0 and 1.6 V, respectively. Higher current in the ohmic conduction region was observed for the N2-facilitated devices, which could be attributed to the lower surface coverage of the perovskite film. A trap limited conduction region (\(m > 2\)) was observed up to 5.0 and 3.2 V for the conventional and N2-facilitated devices, respectively, followed by a pseudo space charge limited region (\(m = 2\)) at higher voltage where carrier recombination is limited by the transport of charges from either the electron or hole transport material or both.\(^{49}\) The sharp current turn-on from the N2-facilitated device indicates that charge injection into the CsPbBr3 layer upon overcoming the energy barrier is far more superior, due to the undulating morphology of the perovskite providing a higher interfacial area for contact with the electron transporting material, thereby explaining the higher charge injection. However, the premature current turn-on voltage as well as the gentle slope in the trap limited conduction region of the conventional device indicate a higher level of defects in the film and lower conductivity of the material as compared to that of the N2-facilitated device.

As compared to the conventional method, devices made with the N2-facilitated film showed substantial improvement in luminance turn-on voltage, \(L_{\text{max}}\) and current efficiency (Table 2). The remarkable turn-on voltage as low as 2.4 V, which is almost comparable to the electronic band gap of the active material (~2.3 eV), means that charge carrier transport and injection into the perovskite emitter are extremely efficient. Despite possessing a higher current turn-on voltage, which signifies a higher carrier injection barrier, the light turn-on voltage for the N2-facilitated devices is lower. This means that once the carriers are injected, they are recombining more effectively, which is explained by the enhanced spatial confinement effect imparted by the smaller grain volumes.\(^{18}\) The current efficiency (Figure 3d) increases with increasing current density and the highest current efficiency was achieved at a high current density (~1000 mA cm\(^{-2}\)), indicating that the efficiency is limited by traps or defects in the device. The champion cell showed an \(L_{\text{max}}\) of 8218 cd m\(^{-2}\) at an astonishingly low voltage of 5.0 V. In contrast, the reference device emitted a much weaker \(L_{\text{max}}\) of 2964 cd m\(^{-2}\). Interestingly, the luminance tripled (based on average \(L_{\text{max}}\)) even though the coverage was slightly reduced (Figure 2b). This improvement is again ascribed to the enhanced radiative recombination bestowed by the spatial constraints that more effectively trap injected charge carriers within the smaller and more isolated grains.\(^{18,27}\) The high brightness at exceptionally low voltages (~5 V) also indicates superb carrier confinement within the perovskite emitter layer.\(^{20}\) At higher voltages, a crossover between the current curves was observed (Figure 3c, current curves), which means that a much higher luminance was achieved at a lower current density for the N2-facilitated device. This is again due to the ease of charge recombination within the smaller domain of each grain, which leads to a huge enhancement in the current efficiency of the N2-facilitated device at a much lower current density (Figure 3d), giving a maximum of 0.718 cd A\(^{-1}\), which is more than 6 times that of the reference device. Future work will entail identifying the dominating process for the drop in voltage across the interface leading to variation in the ideality factor as well as decoupling the impact the deposition technique has on the transport and injection of carriers into the emitter layer. Comparison of EQE was conducted by testing one average device from both experimental methods and plotting the data against the luminance, as shown in Figure 3e. The results show a similar enhancement from 0.020% for the conventional to 0.088% for...
the N₂-facilitated device, indicating lower energy loss and reiterating the importance of the charge confinement effect. The electroluminescence (EL) spectra of both devices measured from 5 to 6 V are plotted in Figure 3b. Similar to the discussion above, the N₂-facilitated device show a several-fold enhancement in the number of counts collected, corresponding to a higher luminance. At low voltage (5 V or less), the EL spectra for the standard and N₂-facilitated device centralize at 526 and 524 nm, respectively, which is in good agreement with the PL spectra of the respective films (Table 1). At higher voltages, a blue shift of 2–3 nm was observed for both EL spectra, resulting in final peaks at 523 and 522 nm. This phenomenon was also previously observed in organometal halide PeLEDs and is likely due to Joule heating during device operation. More in-depth studies on the thermochromic effect in perovskite films have been conducted by Wu et al., relating the phenomenon to electron–phonon renormalization.

To prove that the enhanced device performance is predominantly due to spatial charge confinement within the smaller perovskite grains rather than the thickness difference, additional conventional devices were fabricated by increasing the spin-coating speed to 5000 rpm to achieve an average thickness of 82 nm, which is on par with that of the N₂-facilitated film. Cross-sectional FESEM images as well as device performance data are shown in Figures S3 and S4, respectively, with the characteristic device parameters summarized in Table S1. Here, it is shown that although both films have the same thickness, the N₂-facilitated device still outperforms the conventional one due to the formation of smaller grain structures. Further studies were also conducted to investigate the effect of the pressure of N₂ gas flow and the timing at which it is introduced (additional material characterization and device results can be found in Figures S5–S9). It was found that by further increasing the pressure of the N₂ flow to 2 bar, no improvement in device performance was noted but rather the luminance and current efficiency were somewhat diminished (Table S1 and Figure S8). Although the grain size was reduced with higher N₂ pressure (Figure S6), the poorer device performance is likely ascribed to the additional nonradiative recombination channels formed as a result of the increased surface area of the more isolated grains. The N₂ pressure was then maintained at 1 bar and the timing of the N₂ gas introduction was varied at 1, 3, and 5 s from the start of the spin-coating process. The surface topography (Figure S7) showed negligible difference and all 3 devices gave comparable figures of merit (Table S1 and Figure S9) with an average \( I_{\text{max}} \) turn-on voltage, and current efficiency within 6000–7000 cd m⁻², 2.6–2.7 V, and 0.2–0.3 cd A⁻¹, respectively. It is henceforth concluded that the timing of N₂ introduction is not a critical factor in determining the performance of the N₂-facilitated PeLEDs.

**CONCLUSIONS**

In this work, we have demonstrated the importance of charge confinement in PeLEDs through a solution-processed, N₂-facilitated film formation technique of CsPbBr₃, yielding enhanced EL and efficiency in LED operation. This modus operandi combines the action of rapid supersaturation and pinning of the nucleated crystals to achieve smaller grain sizes and less percolated microstructures. As a result, this led to better spatial confinement of the charge carriers and thus improved radiative recombination and light emission. By optimizing the pressure and timing of the N₂ gas flow, we achieved highly bright PeLEDs (\( I_{\text{max}} = 8218 \text{ cd m}^{-2} \)) with improved efficiencies (current efficiency = 0.718 cd A⁻¹ and EQE = 0.088%) and an extremely low turn-on voltage (\( V_{\text{th}} = 2.4 \text{ V} \)). The type of gas flow is not limited to N₂ and any inert dry gas should accomplish the task. Future work will encompass improving the coverage and compactness of the film morphology to maximize the surface area of light emission. Additional electrical studies will also be performed to investigate what is the limiting carrier and at which interface recombination is taking place in order to further improve the device architecture. This work presents a facile and scalable method to fabricate high-performance PeLEDs, paving a luminous route toward future lighting and display applications.

**EXPERIMENTAL METHODS**

**Device Fabrication.** The devices were made on indium-doped tin oxide (ITO, 7 Ω cm⁻²)-coated glass substrates. Firstly, the substrates were cleaned sequentially using decon soap, deionized water, and ethanol. This was then followed by drying and plasma treatment for 15 min. PEDOT:PSS (Clevios P VP Al 4083) was spin-coated at 4000 rpm for 60 s and annealed for 15 min at 130 °C. The CsPbBr₃ solution was synthesized as previously reported, with a 2:1 molar ratio of CsBr (Aldrich, 99.9%) and PbBr₂ (Aldrich, 99.999%). The chemical precursors were mixed in DMSO solvent (0.5 M concentration) and the clear supernatant was used for all subsequent spin-coating steps. The standard film was spin-coated at 4000 rpm for 30 s and the N₂-facilitated sample was spin-coated at 5000 rpm for 12 s with N₂ gas introduced at a pressure of 1 bar (14.5 psi) from an approximate distance of 2 cm above the spinning substrate. The gas flow was initiated 3 s from the start of the spin-coating process and allowed to continue right to the end. For convenience, the terms “conventional” and “N₂-facilitated” are used to refer to the standard and N₂ gas-facilitated processes in that order. Thereafter, the films were left to dry for 30 min at ambient temperature before annealing at 70 °C for 5 min. Bathophenanthroline (Bphen) (Aldrich, 97%) (25 nm) and aluminum (100 nm) were thermally evaporated to form the electron transporting layer and cathode, respectively. The evaporation was carried out under high vacuum (\(<1 \times 10^{-6} \text{ Torr}\)) and thereafter encapsulated prior to testing. The final cell size was measured to be 7 mm².

**Film and Device Characterization.** All PeLED device characterization was carried out outside the glovebox in ambient conditions. The device characteristics (\(J–V–L\)) and EL spectra were collected using a Keithley 2621B source meter and an OceanOptics QE Pro spectrometer connected to an integrating sphere, operated using Ciemo LabVIEW software. PL measurements were carried out using a Shimadzu RF-S3010 spectrophotometer at an excitation wavelength of 350 nm. The absolute PLQY were measured using an OceanOptics USB4000 spectrometer connected to an integrating sphere and excited using a laser at a wavelength of 405 nm. Time-resolved PL was performed using a streak camera system (Optronis Optoscope). The 400 nm pump pulse was generated by frequency doubling the 800 nm pulse from the regenerative amplifier (Coherent Libra, pulse width 50 fs, repetition rate 1 kHz) using a BBO crystal. All cross-sectional and topological imaging was done using FESEM (JEOL JSM-7600F). The XRD patterns were obtained using an XRD Bruker D8 Advance.

DOI: 10.1021/acs.omega.7b00360
ACS Omega 2017, 2, 2757–2764
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00360.

Current—voltage conduction regimes, additional FESEM images, XRD and PL patterns, optical characterization, and further device performance statistics (PDF)

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the National Research Foundation, Prime Minister's Office, Singapore, under its Competitive Research Programme (CRP Award No. NRF-CRP14-2014-03) and SinBeRISE CREATE programme. T.C.S. acknowledges the financial support from the Singapore Ministry of Education Academic Research Fund Tier 1 grant RG101/15, and Tier 2 grants MOE2014-T2-1-044 and Ministry of Education Academic Research Fund Tier 1 grant CRP14-2014-03) and SinBeRISE CREATE programme. T.C.S. Competitive Research Programme (CRP Award No. NRF-

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