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Precursor Non-stoichiometry to Enable Improved CH₃NH₃PbBr₃ Nanocrystal LED Performance

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Abstract

High photoluminescence quantum yields and narrow emission wavelengths, combined with low temperature solution processing, make CH₃NH₃PbBr₃ nanocrystals (NCs) favorable candidates for light-emitting applications. Herein, we describe the synthesis of CH₃NH₃PbBr₃ NC inks by a convenient room-temperature ligand assisted reprecipitation protocol. We further investigate the effect of modulation of CH₃NH₃Br:PbBr₂ ratio during NC synthesis on the optical properties, crystallinity, particle size distribution and film formation of the NC ink. Subsequently, we fabricate LEDs using these NCs as the emissive layer and the highest efficiency (1.75% external quantum efficiency) and brightness (>2700 cd m⁻²) is achieved for the 1.15:1 precursor ratio. It is inferred that NC surface properties and film coverage are more crucial than photoluminescence intensity to achieve high device efficiency. Moreover, by separating, the NC synthesis and thin film formation processes, we can exert more control during device fabrication, which makes it very promising for scale-up applications.

Introduction

Organic-inorganic hybrid perovskite materials have exceptional properties such as near-unity photoluminescence quantum yields (PLQYs), narrow photoluminescence emission (full width half maximum (FWHM) of ~ 22 nm for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NCs),¹ and convenient tuning of the wavelength of light emission across the visible spectrum, by mere variation of the halide composition.²⁻⁴ Hence, these materials have great potential for achieving high efficiency light-emitting devices such as lasers (both optical and electrically pumped) and light-emitting diodes (LEDs) of the desired wavelengths, including broad white-light emitting LEDs.⁵ Despite the nascency of the field, perovskite-based LEDs have already shown immense progress in device efficiencies, already reaching 10% external quantum efficiency (EQE),⁶ by expanding the knowledge gained from perovskite photovoltaics. The highest efficiency for perovskite-based LEDs to-date have been achieved by creating nanocrystal architectures, via elaborate protocols during the spin coating of the perovskite active layer.⁶⁻⁸ However, judicious manipulation of reaction parameters required during film formation in these protocols, often limits the control over the thin film uniformity and process reproducibility. Decoupling the perovskite NC synthesis from the subsequent thin film formation would allow better control over crystal size and film thickness, thus potentially improving fabrication reproducibility and opening up opportunities for scaling up device fabrication.

$\text{CH}_3\text{NH}_3\text{PbBr}_3$ nanoparticles for LED applications have previously been synthesized by various methods, such as the emulsion synthesis technique for preparing the nanocrystals of different sizes,⁹ HBr addition to obtain nanoplatelet architecture,¹⁰ and fabrication of amorphous nanoparticles with high photoluminescence quantum yields.¹¹ Here, we employed a modified ligand-assisted re-precipitation (LARP) method,³ to synthesize $\text{CH}_3\text{NH}_3\text{PbBr}_3$ nanocrystal (NC) inks exhibiting a NC size distribution of ca. 4-20 nm in diameter. Briefly, the precursors, $\text{CH}_3\text{NH}_3\text{Br}$ and PbBr_2 , were dissolved in small quantities of polar *N,N*-dimethylformamide (DMF) and subsequently injected into non-polar toluene, which acted as anti-solvent to precipitate the NCs. No additional polar solvents were employed to further assist the NC precipitation. In addition, the long carbon chain ligands which passivate the NC surface and control their growth,^{1, 12-15} were pre-mixed in the toluene phase to ensure a uniform dispersion of ligands, while inhibiting the interactions of the precursors with the ligands prior to NC formation. This is in contrast to the conventional LARP method, in which the ligands are added along with the precursors into DMF solvent. Moreover, the ratio of precursors, $\text{CH}_3\text{NH}_3\text{Br}:\text{PbBr}_2$ in the NC synthesis was varied to investigate possible passivation of NC

surface using excess $\text{CH}_3\text{NH}_3\text{Br}$. A similar strategy was effective for direct crystallization of the halide perovskite phase from solution processing methods,⁷ however, its implications for the colloidal LARP synthesis are not yet reported. Here, we examined the effect of precursor non-stoichiometry on the optical properties, crystallinity, particle size distribution, and film formation of the NC ink. LEDs fabricated from the NC inks synthesized from all the investigated precursor ratios showed promising device performances, with a ratio $\text{CH}_3\text{NH}_3\text{Br}:\text{PbBr}_2$ 1.15:1 displaying the highest brightness and efficiency. Moreover, the facile and scalable solution processing techniques involved in the NC ink synthesis and LED fabrication, makes this research promising for large scale device manufacturing processes such as spray coating and inkjet printing.

Experimental

Materials. Methylammonium bromide (Dyesol), lead bromide (TCI), *N,N*-dimethylformamide (DMF; Sigma Aldrich; anhydrous, 99.8%), toluene (Sigma Aldrich; anhydrous, 99.8%), *n*-octylamine (Aldrich; 99%), and oleic acid (Fluka; Ph. Eur) were used to prepare the perovskite NCs. All chemicals were used as received, without any further purification. Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS; Heraeus, Al 4083), 4,6-bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine (B3PYMPM; Lumtec), Ca, and Al, were used as hole-transporting layer (HTL), electron-transporting layer (ETL), and top electrodes, respectively. The electron transport and top electrode materials were stored and handled in Ar atmosphere. UV curing adhesive (Lumtec; epoxy resin/polymer) was used to encapsulate the LEDs.

Synthesis and NC purification. The $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NCs were synthesized by employing the ligand-assisted reprecipitation method. Typically, the methylammonium bromide ($\text{CH}_3\text{NH}_3\text{Br}$; 0.075 mmol; 8.4 mg) and lead bromide (PbBr_2 ; 0.075 mmol; 27.5 mg) precursors were dissolved in 250 μL DMF. Subsequently, this solution was swiftly injected into 5 mL toluene under vigorous stirring, in which an equimolar amount of *n*-octylamine (0.075 mmol; 12.4 μL) and 500 μL oleic acid were mixed prior to the precursors' injection. The amount of $\text{CH}_3\text{NH}_3\text{Br}$ was varied to achieve 1.05:1, 1.15:1, and 1.25:1 precursor ratios. The amounts of PbBr_2 , *n*-octylamine, and oleic acid were left unchanged. All reactions were carried out at room temperature under ambient conditions (60% relative humidity). The reaction was continued for 1 min, after which the obtained colloidal NC solution was centrifuged for 5 min at 6000 rpm.

The supernatant phase, containing unreacted precursors and excess ligands, was discarded. Subsequently, the precipitated NCs were re-dispersed in 1 mL toluene and centrifuged again for 5 min at 1000 rpm. The resulting supernatant phase was used as NC ink for subsequent studies and LED device fabrication.

LED Device Fabrication and Characterization. Pre-etched indium-doped tin oxide (ITO)-coated glass substrates ($8 \Omega \text{ m}^{-2}$) were cleaned sequentially in a soap solution, water, acetone, ethanol, and isopropyl alcohol, after which were these further cleaned by UV ozone for 15 min at 20 °C. Directly after substrate cleaning, approx. 40 nm PEDOT:PSS was spin coated (1 min at 4000 rpm) on the substrate, followed by thermal annealing for 15 min at 130 °C and transferred to an Ar glove box, where the NC inks were spin coated (1 min at 2000 rpm) on the as-deposited PEDOT:PSS layer. Next, the spin coated films were transferred, without further heat treatment, to the evaporation chamber (within the Ar glove box), where 45 nm B3PYMPM (ETL), 7 nm Ca, and 100 nm Al (cathodes) were thermally evaporated. Finally, the resulting devices with an active area of 3 mm² were encapsulated with glass using UV adhesive epoxy resin and characterized under ambient conditions (60% RH). The current-voltage characteristics of the devices were obtained using Keithley 2612B as voltage source. The light emission was collected by an integrating sphere (OceanOptics FOIS-1) coupled to a calibrated spectrophotometer (OceanOptics QEPro).

X-ray Diffraction. X-ray diffraction (XRD) measurements were performed using a Bruker Advance D8 diffractometer with Cu K α radiation, Göbel mirror configuration, and 0.02 rad Soller slit. NC samples were prepared by drop casting the NC ink on glass substrates. The samples were measured from $2\theta = 5\text{-}60^\circ$ with step sizes of 0.02° and 0.5 s per step under a fixed theta value of 1° .

Small Angle X-ray Scattering. Small-angle X-ray scattering (SAXS) measurements were conducted using the Xenocs Nano-inXider, equipped with a Dectris Pilatus3 hybrid pixel detector. This allowed to measure the effective scattering vector magnitude in the range of $0.097 < q < 4.49 \text{ nm}^{-1}$ in SAXS. Samples were measured in sealed glass capillaries (inner diameter 0.95 mm, length 100 mm) under vacuum at room temperature. Particle size distributions were obtained (form-free) from our scattering curves using the Monte Carlo based software package McSAS,¹⁶ using a convergence criterion of 2, with 10 calculating repetitions, and 500 contributions (see Supporting Information for exemplary fits, **Figure S1**).

Microscopy. Selected samples were investigated with a field-emission scanning electron microscopy (FESEM; Jeol 7600F) with an acceleration voltage of 5 kV. For surface morphology studies, the perovskite layer was spin coated (1 min at 2000 rpm) on ITO/PEDOT:PSS and observed without any sputter coating. To determine the thickness of the individual device layers, cross-section images of the ITO/PEDOT:PSS/perovskite NC samples were captured. The samples were sputtered with Pt for 30 s at 30 mA prior to the microscopy studies. The shape, size and crystallinity of the as-synthesized NCs was also confirmed by transmission electron microscopy (TEM). Selected samples were drop-casted on a Cu grid, and dried overnight in a dry box (<30% RH). TEM Images were recorded using a Jeol JEM-2010 microscope operated at 200 kV. AFM imaging was performed on spin coated samples using Asylum Research Cypher S, in repulsive AC mode, using an Al-coated Si tip with a force constant of 42 N m⁻¹ and resonance frequency of 285 kHz.

Absorption and Photoluminescence Spectroscopy. The absorption and steady-state photoluminescence (PL) spectra of the CH₃NH₃PbBr₃ NCs were measured using a Shimadzu UV-2550 spectrophotometer with an integrating sphere attachment (20 nm slit width) and Horiba Fluoromax-4 (slit width 0.4 nm and 0.1 s integration time), respectively. Diluted NC inks (20 µL in 3 mL toluene) were used as the liquid samples. The thin film samples were prepared by spin coating the NC solutions on clean glass substrates (1 min at 2000 rpm). PLQY measurements were performed by exciting thin film samples placed inside an integrating sphere with a 476 nm continuous wave laser. A low pumping intensity of ~0.95 mW cm⁻² was used to avoid Auger recombination effects. Further, time-resolved photoluminescence (TRPL) measurements were conducted by using a 405 nm laser source with low intensity excitation (~2 µJ cm⁻²). The PL signals from the thin films were measured using a time-correlated single photon counter (TCSPC) and analyzed using PicoQuant software. In this case, the NC ink was drop casted on glass substrate to form thin film samples of the NCs.

Photoelectron Spectroscopy. The elemental composition of spin coated NC thin films on ITO substrates (1 min at 2000 rpm) were determined by X-ray photoelectron spectroscopy (XPS). The XPS signal is excited by monochromatic Al K-alpha (hν = 1486.7 eV) and detected by electron analyzer (Omicron, EA125). The analyzer work function is calibrated using Au Fermi edge. Valence band maxima (VBM) of drop casted NC solutions on ITO substrates were

determined by photoelectron spectroscopy in air (PESA) using Riken Photoelectron Spectrometer (Model AC-2). The conduction band minima (CBM) were calculated through addition of the optical band gap and VBM.

Results and discussion

$\text{CH}_3\text{NH}_3\text{PbBr}_3$ NC inks were first synthesized from a stoichiometric ratio of precursors, by a modified LARP method, as discussed in Experimental section. The instantaneous change of the transparent toluene solution, into a greenish-yellow colloidal solution, upon precursor addition, indicated the formation of ligand-capped NCs.^{3, 17} No additional reagents, like butanol, acetone, or γ -butyrolactone,^{11, 17-19} were required to further assist the NC precipitation. The NC ink obtained after purification was bright and fluorescent green, signifying formation of highly luminescent NCs (inset **Figure 1a**). The absorption and photoluminescence (PL) spectra, revealed an absorption edge and PL maximum at ~ 531 nm and 522 nm, respectively, (black curve, Figure 1a,b), similar to reported values for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NCs.^{20, 21} The PL peak exhibits a full width half maximum (FWHM) of 21 nm, which indicates high color saturation favorable for display applications.³

The phase-purity of the NCs was determined from X-ray diffraction (XRD) measurements. The XRD patterns (black curve, Figure 1c) clearly shows the characteristic perovskite $\text{CH}_3\text{NH}_3\text{PbBr}_3$ peaks at 14.9° , 21.1° , 30.1° , 33.7° , 36.9° , 43.2° , and 46.1° which correspond to the (100), (110), (200), (210), (211), (220), and (300) planes, respectively.^{7, 19} This corresponds to the cubic phase with lattice constant 5.94 Å and $Pm-3m$ space group.^{19, 22} The *n*-octylamine ligand used in the NC synthesis may also form a 2D layered octylammonium bromide structure, concurrently to the 3D $\text{CH}_3\text{NH}_3\text{PbBr}_3$ phase resulting in diffraction peaks below $2\theta = 10^\circ$.²³ The absence of such additional peaks in the diffractograms indicate that phase-pure $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NCs were fabricated from the stoichiometric precursor solutions.

Figure 1. Optical and structural characterization of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NCs synthesized from the different molar ratios of $\text{CH}_3\text{NH}_3\text{Br}:\text{PbBr}_2$, 1:1 (black), 1.05:1 (red), 1.15:1 (blue), and 1.25:1 (magenta). **(a)** Steady-state PL spectra (normalized to absorbance at the excitation wavelength) of the spin-coated NC thin films. The inset shows images of the NC ink under white light (left) and UV light (right), respectively. **(b)** Absorbance of the NC inks **(c)** XRD patterns of drop-casted NC films.

The effect of excess $\text{CH}_3\text{NH}_3\text{Br}$ during the NCs synthesis was investigated using various ratios of $\text{CH}_3\text{NH}_3\text{Br}:\text{PbBr}_2$ in the precursor solution, specifically 1.05:1, 1.15:1, and 1.25:1, while keeping other reaction parameters and the centrifugation procedure unchanged. (i.e. similar to reactions carried out with stoichiometric ratio). The NC inks exhibited similar bright green fluorescence for all tested stoichiometries, although it should be mentioned that for ratio 1.25:1 the NC ink appeared cloudy and less stable.

X-ray diffraction patterns of the samples were then analyzed to investigate the effect of excess $\text{CH}_3\text{NH}_3\text{Br}$ on the as-formed nanocrystals' phase and crystal structure. All tested precursor ratios displayed the characteristic cubic perovskite peaks, without the formation of secondary phases. The crystal phase and crystalline nature of the NCs was thus retained upon changing the precursor ratios (**Figure 1c**). While no significant peak shifts were observed in the diffractograms, slight variations in the FWHM of the peaks were observed. The average crystallite size, as calculated from the Scherrer equation, were 11.3 nm, 11.6 nm, 13.6 nm and 12.3 nm, respectively for ratios 1:1, 1.05:1, 1.15:1 and 1.25:1. This suggests that excess $\text{CH}_3\text{NH}_3\text{Br}$ did not affect the crystal lattice, and only slightly influenced the NC sizes. This corroborates with the results obtained in case of using excess $\text{CH}_3\text{NH}_3\text{Br}$ during direct formation of perovskite NC by spin coating the precursor solution to form thin films, as demonstrated by Cho et al.⁷ Subsequent X-ray photoelectron spectroscopy (XPS) measurements showed a Br deficiency on the NC surface for all tested stoichiometries, with Pb:Br of ca. 2.6-2.7, similar to that reported by Gonzalez-Carrero et al.¹⁹ (**Figure S2, Table S1** - see Supporting Information).

The NCs synthesized using non-stoichiometric precursor ratios showed different ink concentrations (i.e. NC yield, **Figure S3** - See Supporting Information) compared to stoichiometric synthesis. This is clearly observed in the absorbance spectra of the NC inks (Figure 1b). Although all samples displayed a similar absorption edge ranging 531-534 nm (ca. 2.3 eV optical band gap), the absorbance was significantly lower for the 1.25:1 ratio. This may be related to the lower colloidal phase stability (i.e. cloudy NC ink with precipitate), and

consequently lower NC yield after purification. Next, the PL of the NCs inks was studied as an important indicator for the electroluminescence (EL) in light-emitting devices. A comparison of the spin-coated thin films prepared from all tested CH₃NH₃Br:PbBr₂ ratios, displayed a similar maximum PL emission and FWHM of approximately 522.7 ± 0.1 nm and 22.2 ± 0.1 nm, respectively (**Table S2** - See Supporting Information). The PL intensity was corrected for the differences in absorbance at the excitation wavelength using $PL_{corr} = \frac{PL}{1-(10^{-Abs})}$, to fairly compare the PL from the various samples (Figure 1a). A slight excess of CH₃NH₃Br:PbBr₂ = 1.05:1 displayed the highest PL, indicating improved radiative recombination, while increased CH₃NH₃Br amounts led to decline in the PL intensity. The decrease in PL at higher CH₃NH₃Br:PbBr₂ ratios may be due to replacement of capping ligands by the excess CH₃NH₃⁺ ions,²⁴ which may adversely affect charge confinement and thereby reduce radiative recombination. Moreover, excessive amounts of CH₃NH₃Br can de-stabilize the colloidal solution, as observed in case of 1.25:1 ratio. The PLQY values displayed a similar trend as observed in the PL spectra, with 42.7%, 61.8%, 57.3%, and 40.3% for CH₃NH₃Br:PbBr₂ = 1:1, 1.05:1, 1.15:1, and 1.25:1, respectively.

Next, the size distribution of the NC inks (in solution phase) was investigated by means of small angle X-ray scattering (SAXS). Interestingly, a bimodal size distribution was observed with peaks centered roughly at 6 nm and 18 nm mean diameter for all investigated samples (**Figure 2a**). To confirm whether the size distribution is retained after solvent evaporation (i.e. in thin film), the particle size distribution was also determined from the low-magnification TEM images of the 1.15:1 sample (Figure 2b,c). The size distribution obtained from the TEM image corresponds well with the values extracted from the scattering curves. Moreover, the average nanocrystal sizes obtained from the TEM image matches well with the average sizes obtained from XRD. It is noticed that the average NC sizes in the solution phase are slightly larger than that in films. This could be due to the dynamic nature of the ligand attachment and separation in the solution,¹³ which may affect the sizes measured with SAXS.

Figure 2. (a) Particle size distribution of the NC ink, extracted from the small angle X-ray scattering measurements, for the $\text{CH}_3\text{NH}_3\text{Br}:\text{PbBr}_2$ NCs synthesized from $\text{CH}_3\text{NH}_3\text{Br}:\text{PbBr}_2$ ratios of 1:1, 1.05:1, 1.15:1, and 1.25:1. (b) TEM image of NC ink prepared from 1.15:1 precursor, drop casted on Cu grid. The inset is the SAED images clearly showing the polycrystalline nature of the NCs. (c) Particle size distribution extracted from the above TEM image, at least 100 NCs were measured.

To investigate the effect of precursor non-stoichiometry on the NC surface passivation, time-resolved photoluminescence (TRPL) measurements were performed. The PL decay kinetics, after photoexcitation from a pulsed laser, reveal the nature of the radiative recombination. The recombination lifetimes were obtained from bi-exponential fitting the TRPL decay curves. The fit function is: $I(t) = A_f e^{-\frac{t}{\tau_f}} + A_s e^{-\frac{t}{\tau_s}}$, where τ_f and τ_s are the fast and slow decay lifetimes, respectively, and A_f and A_s are their respective decay amplitudes. The average lifetime is calculated as $\tau_{avg} = A_f \tau_f + A_s \tau_s$. Generally, fast decay represents the trap-assisted recombination at the crystal surface and the longer-lifetime component represents radiative recombination inside the crystals.²⁵ Herein, average decay times of 5.52 ns, 5.49 ns, 6.30 ns and 8.36 ns were estimated for the 1:1, 1.05:1, 1.15:1 and 1.25:1 ratios of $\text{CH}_3\text{NH}_3\text{Br}:\text{PbBr}_2$, respectively (**Figure 3, Table 1**). The short average lifetimes (<10 ns), are indicative of the large number of grain boundaries, which may act as traps in the NC film. However, the relative contribution of the trap-assisted recombination component, A_f , decreased from ca. 42 % for both 1:1 and 1.05:1 ratios, to approximately 32 % for 1.15:1. The

decrease in A_f value may indicate a slight reduction in number of trap states due to improved surface defect passivation by the excess $\text{CH}_3\text{NH}_3\text{Br}$. Moreover, if we calculate the volume of the NCs from the average crystallite size determined from the Scherrer equation, there is a ~75% crystallite volume increase for the 1.15:1 $\text{CH}_3\text{NH}_3\text{Br}:\text{PbBr}_2$ compared to the 1:1 ratio, despite the minor increase in crystallite size (13.6 nm compared to 11.3 nm, respectively). This increase in NC volume implies a 20% decrease in surface-to-volume ratio for the former, which could significantly lower the contribution of surface traps to the recombination in the NC films. It is noted that the amplitude of the trap-assisted decay component is similar to the 1.15:1 ratio for the 1.25:1 $\text{CH}_3\text{NH}_3\text{Br}:\text{PbBr}_2$ ratio, however, the low colloidal stability of the latter makes it less promising for LED applications.

Figure 3. TRPL spectra of NCs prepared by varying the $\text{CH}_3\text{NH}_3\text{Br}:\text{PbBr}_2$ ratios viz. 1:1 (black), 1.05:1 (red), 1.15:1 (blue), and 1.25:1 (magenta).

Table 1. Recombination lifetimes obtained from bi-exponential fitting of the TRPL decay curves.

Ratios	τ_f (ns)	A_f (%)	τ_s (ns)	A_s (%)	τ_{avg} (ns)
1:1	1.60	43	8.43	57	5.52
1.05:1	1.53	42	8.40	58	5.49
1.15:1	1.52	32	8.55	68	6.30
1.25:1	1.97	35	11.84	65	8.36

Light-emitting diodes (LEDs) were fabricated using the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NCs prepared from the different precursor ratios of $\text{CH}_3\text{NH}_3\text{Br}:\text{PbBr}_2$. A device structure with ITO / PEDOT:PSS / $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NC / B3PYMPM (45 nm) / Ca (7nm) / Al (80 nm) was used. Here, the PEDOT:PSS and the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NC layers were spin coated, while the subsequent charge transport layers were thermally evaporated. Cross-sectional imaging of the

ITO/PEDOT:PSS/ $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NC stack, under a scanning electron microscope (SEM), showed ~ 30 nm of PEDOT:PSS layer and ~ 40 nm NC layer (**Figure S4**). The top view SEM imaging revealed that the nanoparticle morphology was retained in the thin film (Figure S4). The flat-band energy level diagram for the complete LED device stack is depicted in **Figure S5**. Valence band maxima (VBM) for the NCs, ca. 5.6 eV for all samples, calculated from photoelectron spectroscopy in air (PESA) (Figure S5), correspond well with previous reports for $\text{CH}_3\text{NH}_3\text{PbBr}_3$.²⁶ The PEDOT:PSS and B3PYMPM layers acted as good hole and electron transport layers, with a work function (WF) of 4.9 eV,²⁷ and lowest unoccupied molecular orbital (LUMO) level of ca. 3.4 eV,²⁸ respectively. The WF has an offset of ~ 0.7 eV with the NC VBM, whereas the LUMO level has a 0.1 eV offset with the NC conduction band minimum (CBM). Here, the CBM value was calculated through the addition of the optical band gap of 2.3 eV to the VBM value.

The device performances are shown in **Figure 4**. All the devices displayed a turn-on voltage (defined as voltage required to reach 1 cd m^{-2}) of 2.7-2.8 V. The turn-on voltage is higher than the optical band gap of 2.3 eV, but lower than previously reported for $\text{CH}_3\text{NH}_3\text{PbBr}_3$ nanoparticle LEDs.⁹⁻¹¹ The turn-on voltage is dependent on the transport layers used,¹⁷ and may be further lowered by employing transport layers which provide better charge injection and charge confinement. The J-V-L curves also reveal low leakage currents ($\sim 10^{-4} \text{ mA cm}^{-2}$), in all the devices. The low turn-on voltages and leakage currents are indicative of good injection of carriers (no significant injection barrier due to the ligands) as well as good surface coverage of the NCs (no shunt paths).

Figure 4. LED characterization **(a)** Current density-voltage-luminance (J-V-L) curves of the devices – the solid lines represent the J-V curves while the dashed lines represent the L-V curves. The inset shows a representative image of our LED device. **(b-d)** Current efficiency (CE), power efficiency (PE) and external quantum efficiency (EQE) plot, respectively, of the devices as a function of luminance. The black, red, blue and magenta curves correspond to the 1:1, 1.05:1, 1.15:1, and 1.25:1 ratios of CH₃NH₃Br:PbBr₂ respectively.

As shown in Figure 5, the 1.15:1 ratio of CH₃NH₃Br:PbBr₂ displayed the highest luminance among all fabricated devices, with a maximum luminance of 2721 cd m⁻² at 5.6 V. The same device also exhibited the best current efficiency of 6.45 cd A⁻¹, obtained at 3.4 V and 93.8 cd m⁻² luminance the maximum EQE obtained was 1.75%. The performance of the best device compared to other colloidal CH₃NH₃PbBr₃ NC LEDs reported in literature is summarized in **Table S3** – See Supporting Information. It is interesting that despite a lower PL intensity compared to the 1.05:1 ratio, the EL intensity and device efficiency was higher for the 1.15:1 ratio. This could be related to the lower trap-assisted recombination in the 1.15:1 ratio samples, as determined with TRPL. In addition, the morphology of the NC film can critically influence the device performance.^{7, 29}

To examine the surface morphology of the NC films, atomic force microscopy (AFM) was used. A 3D view of the AFM images clearly depicts non-uniform NC coverage for all investigated samples (**Figure 5a**). We postulate that the large gaps (violet to pink color) observed in the images are in fact a layer of NCs. In case of pin hole formation, high leakage currents and shunt paths are expected.^{14, 30} The absence of any additional resistances in the J-V curve (Figure 4a) and good diode behavior, thus suggests that the nanocrystals form a sufficiently dense film. Nevertheless, the CH₃NH₃Br:PbBr₂ 1.05:1 and 1.25:1 ratios showed poor thin film uniformity, as illustrated by large areas of low NC film height (violet to pink color) in the respective NC thin films. The surface morphology appears, relatively less non-uniform for the 1:1 and 1.15:1 ratios. To more accurately compare the surface morphologies of the 1:1 and 1.15:1 ratios, were examined using height profiles extracted from the 2D AFM top-view images. (Figure 5b,c). Clearly, the height variation for the 1.15:1 ratio is less than observed for the 1:1 ratio, which could lead to more concentrated recombination, and consequently, to higher electroluminescence in the CH₃NH₃Br:PbBr₂ 1.15:1 sample.

Figure 5. (a) 3D view of AFM images of thin films of NCs prepared by varying the $\text{CH}_3\text{NH}_3\text{Br}:\text{PbBr}_2$ ratios viz., 1:1, 1.05:1, 1.15:1, and 1.25:1. Comparison of 2D AFM images and height profiles of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NC thin films prepared from (b) 1:1 and (c) 1.15:1 ratio of $\text{CH}_3\text{NH}_3\text{Br}:\text{PbBr}_2$. The horizontal black lines in the images indicate the position of height profile measurement.

Conclusion

Highly luminescent $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NC inks, with a bimodal particle size distribution, were synthesized through a modified LARP synthesis protocol. The $\text{CH}_3\text{NH}_3\text{Br}:\text{PbBr}_2$ ratio in the precursor solution was varied to 1.05:1, 1.15:1, and 1.25:1. The influence of the precursor non-stoichiometry on the optical and structural properties of the NCs, as well as the implications for NC film formation and subsequent LED performances were evaluated. The cubic perovskite crystal structure and the NC sizes were virtually unaffected by the addition of excess $\text{CH}_3\text{NH}_3\text{Br}$; however, the optical properties and the NC film surface morphologies, were significantly influenced. Interestingly, while the PL intensity was highest for the NCs formed from 1.05:1 ratio of $\text{CH}_3\text{NH}_3\text{Br}:\text{PbBr}_2$, EL intensity was highest for the 1.15:1 ratio. The higher

electroluminescence for the 1.15:1 precursor ratio, could be attributed to higher NC density in the spin-coated films as well as the reduction in trap-assisted recombination, compared to the other investigated precursor ratios. The NC surface properties and film coverage were found to be more critical than high PL in the NCs for achieving high EL in devices. Notably, the LEDs prepared from the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NC inks, synthesized from a 1.15:1 precursor ratio, achieved a maximum EQE of 1.75%, which is among the best reported efficiencies for colloidal $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NC-based LEDs.

Conflicts of interest

There are no conflicts of interest to declare.

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