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Cesium Lead Halide Perovskite Nanocrystals Prepared by Anion-exchange for Light-Emitting Diodes

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ABSTRACT. Cesium lead halide perovskite nanocrystals (NCs) have emerged as a promising emitter for lighting and display technologies. However, the iodide containing CsPb(Br/I)₃ and CsPbI₃ NCs suffer from chemical and phase degradation to non-functional orthorhombic (δ) phase. To address this challenge, we developed a facile synthetic protocol for halide exchange in pristine CsPbBr₃ NCs. The protocol involves change in the nucleophilicity (or basicity) of the halide ions in aqueous-organic media which acts as the driving force to facilitate the halide exchange. Our method avoids the use of additives for anion solubilization, which otherwise induces chemical

instability and quench the emission. The halide exchanged $\text{CsPb}(\text{Br/I})_3$ and CsPbI_3 NCs showed enhanced structural and optical properties, such as high phase stability and emission quantum yields up to 94.2% as compared to the NCs (of same composition) obtained from direct synthesis. In addition, we demonstrated fabrication of light emitting devices (LED) based on halide exchanged $\text{CsPb}(\text{Br/I})_3$ and CsPbI_3 NCs. The devices showed peak external quantum efficiency (EQE) of 1.9% with a peak wavelength of 670 nm and low luminance turn-on voltage of 2.5 V.

INTRODUCTION

Recent years have witnessed the emergence of solution-processable lead halide perovskites as the most sought-after materials for application in optoelectronics such as solar cells, light emitting diodes (LED), lasing and display devices.¹⁻⁴ Lead halide perovskite exhibits unique photophysical and optoelectronic properties and has the additional advantage of solution processability, low cost and are easy to scale-up.^{5,6} Further, the colloidal form of lead halide perovskite nanocrystals (NCs) posses excellent luminescent properties such as near-unity emission quantum yield (QY), narrow-band emission, high color purity, color tunability based on size and composition etc. which lead to their widespread applications, particularly in visible and near-infrared LEDs.^{3,4,7}

So far, the highest external quantum efficiency (EQE) has been >20% as reported in the case of green emitting $\text{CsPbBr}_3/\text{MABr}$ quasi-core/shell structure, red emitting $\text{CsPb}(\text{Br/I})_3$ NCs and near-infrared emitting amine-functionalized FAPbI_3 thin film perovskite LED.⁸⁻¹⁰ However, as a general trend, compared to green, only few reports are available on red LEDs.¹⁰⁻¹⁷ Lead iodide perovskites such as APbI_3 NCs (where, $\text{A} = \text{CH}_3\text{NH}_3^+/\text{Cs}^+/(\text{NH}_2)_2\text{CH}^+$) are promising materials due to their relatively low band gaps with absorption towards the longer wavelength. However, such organic-inorganic hybrid iodide perovskites suffer from intrinsic chemical instability issues,

either due to photo-degradation or exposure to moisture.¹⁸ Particularly, the organic cation in the organic-inorganic hybrid perovskite is hygroscopic and readily decomposes the crystal lattice structure.¹⁹ Although, the all-inorganic CsPbI₃ perovskite outperforms,²⁰ the cubic phase (α -CsPbI₃) transits into non-functional orthorhombic phase (δ -CsPbI₃), which practically restrains their application.²¹ Efforts to stabilize the α phase mainly focusses on alloying and doping with various divalent and heterovalent metal ions,²²⁻²⁵ halide (Br⁻ and Cl⁻) ions,²⁶ incorporation of larger organic cations¹⁶ and surface passivation.^{11, 21, 27} However, partially replacing either the Pb²⁺ or I⁻, significantly changes the band gap. Besides, the ligand-protected mixed halide CsPb(Br/I)₃ NCs have certain limitations due to their dynamic surface chemistry.²⁸ It is widely known that as more I⁻ ions are introduced into the crystal lattice of CsPbBr₃, which is favoured by the inherent mass action, the lattice constant increases²⁹ and the surface of nanocrystals undergoes reconstruction to lower the surface energy, consequently more surface defects are formed.^{29, 30} Further, the ligand binding efficiency on the surface of NCs changes as I⁻ ions are softer than Br⁻ ions.^{29, 31} It has been reported that ligand density is significantly reduced in CsPbI₃ NCs, as confirmed by 1D and 2D ¹H NMR, which otherwise makes the NCs more insulating.²⁹

Typically, all-inorganic iodide-based NCs are synthesized either through hot-injection method⁷ or halide exchange in pre-synthesized CsPbBr₃ NCs in solution and thin films.^{31, 32} Halide ions are easily exchangeable,^{7, 31} while preserving the cationic sub-lattice and cubic shape of the NCs.³³ Traditionally, halide exchange is done by using metallic halide salts (of Pb, Sn, Zn, Li, and lanthanides), dissolved in polar solvents^{20, 34-37} or using Grignard or trimethylsilyl reagents.³⁸ The use of long chain organic ammonium halides and tetrabutylammonium halides as precursors have also been reported.¹⁰ However, such process requires tedious synthesis of halide precursors.^{31, 32} Similarly, the presence of excess precursors and ligands in halide exchange reaction can cause

destabilization of the desired perovskite phase which impede the charge carrier injection and transport at the interface of devices.^{11,36,21} In addition, the presence of any metal ions (extrinsic impurity) or residual polar solvents (used during halide exchange) may impart adverse effects on the structural and photophysical properties of perovskite NCs.^{39,40} For example, quenching in the emission intensity, change in morphology, and phase instability of iodide-based NCs due to these residues, have been reported earlier.⁴¹ Hence, developing a facile methodology that addresses such synthetic challenges is required. Our goal is to obtain CsPbI₃ NCs with superior structural and photophysical properties suitable for a broad spectrum of applications.

Herein, we report the development of a new post-synthetic halide exchange method to obtain CsPbI₃ nanocrystal (NCs), as shown in Scheme 1. We used water as a medium to transfer the iodide ion present in formamadenium iodide (FAI) to the CsPbBr₃ NCs (in toluene) to replace bromide with iodide ions. Polar solvents like methanol and ethanol also act as suitable solvent for solubilizing FAI. However, these solvents are miscible with toluene and hence an interface chemistry based on layer separation is not possible. Even meagre amount of polar protic solvent can protonate the capping ligands and cause their desorption from the surface of NCs.²⁹ The CsPb(Br/I)₃ and CsPbI₃ NCs thus obtained are free from excess ligands and other impurities, which could be the reason for their high emissivity and longer stability observed in solution, as well as in thin films.²¹ LEDs based on these NCs as active layer showed a luminance turn-on around 2.5 V, which is clearly indicating the minimum resistivity of these NCs.

Scheme 1. A schematic representation of the synthesis of CsPbI₃ NCs from CsPbBr₃ NCs using formamidinium iodide (FAI) in water as the Iodide source.

EXPERIMENTAL SECTION

Chemicals

Cesium carbonate (99%), lead (II) bromide (98+%), oleic acid (reagent grade 99 %), oleylamine (technical grade 70%), 1-Octadecene (technical grade, 90%), toluene (anhydrous, 99.8%), 1-butanol (anhydrous, 99.8%), methyl acetate (anhydrous, 99.5%), acetonitrile (anhydrous, 99.8%), tetrabutylammonium iodide (>99%), and tetrabutylammonium chloride ($\geq 97.0\%$) were procured from Sigma Aldrich. Formamidinium iodide and methyl ammonium iodide were purchased from Dyesol Limited (now known as GreatCell Solar). All chemicals were used as purchased without further purification.

Synthesis of CsPbBr₃ NCs

CsPbBr₃ NCs were prepared by adapting a two steps synthetic protocol reported by Protesescu et al.⁷ The first step involved synthesis of cesium oleate. For this, 0.203 g (0.62 mM) of cesium

carbonate along with 650 μL of oleic acid was added to 10 ml octadecene, taken in a two-neck round bottom flask. The reaction mixture was heated to 120 $^{\circ}\text{C}$ under vacuum with continuous stirring for 1 hour. Subsequently the mixture was purged with N_2 gas to obtain cesium oleate.

In the second step, 0.276 g (0.752 mM) of PbBr_2 along with oleic acid and oleylamine (2 ml, each) were added into a two-neck round bottom flask containing 20 mL of octadecene and the mixture was heated to 120 $^{\circ}\text{C}$ for 1 hour under vacuum with continuous stirring. After 1 hour, vacuum was stopped and the temperature was raised to 180 $^{\circ}\text{C}$ under continuous N_2 gas purging. To this, about 1.6 mL of cesium oleate prepared in the first step (pre-heated to 120 $^{\circ}\text{C}$) was swiftly injected and the reaction flask was immediately cooled to room temperature by placing it in an ice-water bath.

Isolation and purification of CsPbBr_3 NCs

The CsPbBr_3 NCs in octadecene were isolated by adding 10 ml of 1-butanol (toluene: butanol=2:1), followed by centrifugation at 8000 RPM for 10 minutes. The clear supernatant was discarded, and the precipitate was re-dispersed in 20 ml of anhydrous toluene with a final concentration of 10 mg per mL. A second centrifugation is done at 3000 RPM for 5 minutes to discard the bigger nanoparticles and agglomerates. It must be noted that the NCs are washed with 1-butanol, a stronger polar protic solvent, to get rid of the excess ligands, which otherwise makes thin film appear oily, when spin coated. Presence of excess ligands also impacts the devices fabricated from those NCs, which does not respond well to electric signals.

Halide exchange using formamidinium iodide (FAI)

We used three different concentrations (0.0242 mM, 0.0436 mM and 0.058 mM) of formamidinium iodide (FAI) for the exchange reaction. The washed CsPbBr_3 NCs were re-

dispersed in toluene with a concentration of 10 mg/mL and used the same for the halide exchange reaction. Water to toluene (containing the NCs) ratio was maintained at 1:2. For this, we took 1 ml of CsPbBr₃ NCs in toluene and 500 μ L of water and to that 25 mg (0.0242 mM) of FAI powder was added. This mixture was vigorously mixed (using vortex) for less than a minute to allow the iodide replacement to take place. After completion of the reaction, the 1 ml of CsPb(Br/I)₃ NCs in toluene was separated from the water phase by centrifuging at 5000 RPM for 5 minutes. The bottom part i. e. water along with other by-products was discarded. The top part i.e. 1 mL of CsPb(Br/I)₃ NCs in toluene was washed one more time with 500 μ L of anhydrous methyl acetate (toluene: methyl acetate ratio is 2:1) followed by centrifugation at 8000 RPM for 5 minutes. The final precipitate obtained was then re-dispersed in 1 mL of anhydrous toluene. This was then used for further measurements. To incorporate more I ions into the CsPbBr₃ NCs, the concentration of FAI was increased to 45 mg (0.0436 mM) and 60 mg (0.058 mM) for treatment with 1 ml of CsPBr₃ NCs in toluene and 500 μ L of water, and followed the same steps, as mentioned earlier.

Formamidinium Bromide (FABr) Treatment of CsPbBr₃ NCs

A control experiment was done to check if FA⁺ is getting incorporated to the CsPbBr₃ NCs. For this, about 50 mg (0.04 mM) of FaBr was added to 1 ml of CsPbBr₃ NCs in toluene and 500 μ L of water. This mixture was vigorously shaken and the toluene/water layers were separated by centrifugation at 5000 RPM for 5 min. The NCs in toluene were washed with 500 μ L of methyl acetate and finally the NCs obtained were re-dispersed in toluene.

Halide exchange using Tetrabutylammonium iodide (TBAI)

About 4.3 mg (0.012 mM) and 8.7 mg (0.0236 mM) of TBAI was weighed and added separately to 1 ml of CsPbBr₃ NCs in toluene and 500 μ L of water. The mixture was vigorously shaken and then separated the water and toluene layers by centrifugation at 5000 RPM for 5 minutes. The water containing the by-products was discarded and the top toluene layer containing the CsPb(Br/I)₃ was washed with 500 μ L of methyl acetate. The method of washing was same as in FAI treatment.

Halide exchange using methyl ammonium iodide (MAI)

Three different concentrations of MAI i. e. 3.8 mg (0.0242 mM), 6.9 mg (0.0436 mM) and 9.2 mg (0.058 mM) were used, each added separately to 1 ml of CsPbBr₃ NCs in toluene and 500 μ L of water following the same procedure.

Halide exchange using Tetrabutylammonium chloride (TBA-Cl)

We used two different concentrations of TBA-Cl; 6.67 mg (0.024 mM) and 10 mg (0.035 mM), each of which is added to 1 ml of CsPbBr₃ NCs dispersed in toluene and 500 μ L of water. The procedure was same as in FAI treatment, except that here we used mild shaking since high speed mixing using vortex caused degradation of the NCs.

Direct synthesis (by hot-injection method) of CsPbI₃ and CsPb(Br/I)₃ NCs nanocrystals

0.087 g (0.188 mM) of PbI₂ along with 5 ml of octadecene, 500 μ L each of oleic acid and oleylamine were added into a 3 neck round bottom flask. The mixture was heated to 120 $^{\circ}$ C under vacuum with continuous stirring for one hour. When the PbI₂ dissolved completely, the temperature was raised to 160 $^{\circ}$ C and 400 μ L of cesium oleate (pre-heated to 120 $^{\circ}$ C) was swiftly

injected to this. The reaction flask was immediately cooled to room temperature by placing it in an ice-water bath. The NCs obtained were isolated from octadecene by centrifugation at 8000 RPM for 10 minutes and re-dispersed the precipitate in 10 ml of anhydrous toluene. Acetonitrile was used as anti-solvent to wash the as-synthesized CsPbI₃ NCs to get rid of the excess ligands, for this 5 ml of anhydrous acetonitrile was added to the above, followed by centrifugation at 8000 RPM for 5 min. The precipitate obtained after centrifugation is re-dispersed in 5 mL of anhydrous toluene

For hot-injection synthesis of CsPb(Br/I)₃ NCs, 0.074 g (0.16 mM) of PbI₂ and 0.01 gm (0.028 mM) of PbBr₂, along with 5 ml of octadecene, 500 μ L of each of oleic acid and oleylamine were added into a 3-neck round bottom flask. Other reaction conditions and purification steps were similar to that of CsPbI₃ NCs.

Characterization of NCs

UV-vis absorption and PL spectra were collected using Shimadzu UV1800 UV-VIS Spectrophotometer and Horiba Fluoromax, respectively. X-Ray diffraction patterns were recorded using XRD Bruker D8 Advance and TEM images with Tecnai (model: FEI Tecnai F20). The absolute PLQY was measured with the sample in an integrating sphere, and the emission was collected with charge-coupled device array (Princeton Instruments, Pixis) coupled to a monochromator (Acton, Spectra Pro). Time-resolved PL was performed using a streak camera system (Optronis Optoscope). Solution ¹H NMR experiments were recorded at 9.40 T (ν_0 (¹H) = 400.13 MHz) using a Bruker Avance I 9.40 T spectrometer with a Bruker 5 mm BBO probe. The ¹H experiments employed a one-pulse sequence, with a $\pi/2$ pulse length of 10 μ s and a

recycle delay of 1 s. Samples were prepared with toluene-d8 solvent and were referenced internally.

LED Device fabrication and characterization

Pre-etched indium-tin oxide on glass substrates (ITO; sheet resistance $\sim 8 \Omega \text{ cm}^{-1}$) are obtained from Wuhan Jinge Solar Energy Technology Co., Ltd) and used as-purchased. The substrates are sequentially washed in detergent solution, acetone, ethanol, and 2-propanol in an ultrasonication bath. Before the spin coating of PEDOT:PSS (Clevios 4083; filtered with $0.45 \mu\text{m}$ PVDF filter, 1 min at 4000 rpm), the dried ITO substrates was treated with UV ozone for 20 mins. The deposited PEDOT:PSS films were annealed at 130°C for 10 min to remove the residual solvent before. The perovskite nano-crystal (dispersed in toluene, $\sim 5 \text{mg ml}^{-1}$) are then spin coated on PEDOT:PSS (500 rpm for 60 seconds) in the inert glovebox environment. The electron transporting layer (POT2T, 2,4,6-Tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine, 45 nm) and cathode (Ca and Al, 7nm and 100 nm, respectively) are subsequently thermally evaporated at high vacuum ($< 5 \times 10^{-6}$ mtorr). The active area of the devices are 3 mm^2 . The devices are encapsulated in the glovebox and characterized in ambient environment. A Keithley 2612B was used to obtain the current-voltage characteristics of the LED devices using a scan rate of 1 V s^{-1} (step size 0.1 V, step interval 0.1 s). The light emission was collected by an integrating sphere (OceanOptics FOIS-1) coupled to a calibrated spectrophotometer (OceanOptics QEPro).

RESULT AND DISCUSSION

The CsPbBr_3 NCs used in our halide exchange method was prepared by following a hot-injection synthesis as reported in the literature.⁷ The halide exchange process in those bromide NCs solution

was carried out under ambient conditions, through a facile and green method. The as-synthesized CsPbBr₃ NCs were first washed with 1-butanol to remove unreacted precursor and excess ligands, the details of synthesis, isolation and purification procedure of CsPbBr₃ NCs are mentioned in the experimental section. Next, 1 ml of CsPbBr₃ NCs (re-dispersed in toluene, having a concentration of 10 mg/mL) along with 500 μ L of water were treated with different amounts of perovskite precursor-formamidinium iodide (FAI), as mentioned in the experimental section. Here, FAI acts as iodide source to facilitate halide ion exchange in CsPbBr₃ NCs. We hypothesize that the water would dissociate the FAI molecule to FA⁺ and I⁻ ions, in which the later would subsequently be transferred to the toluene phase to replace the Br⁻ ions in the CsPbBr₃ NCs. This exchange is facilitated through changes in the base strength of I⁻ in both aqueous and toluene media.

Note that although exposure to humidity or rather adsorption or diffusion of water is known to be detrimental to the crystal structure of halide perovskites,^{39, 42} in our method, the CsPbBr₃ NCs capped with oleic acid (OA) and oleylamine (OLA), are re-dispersed in toluene. Since water and toluene are completely immiscible, these NCs are fully protected from any water or moisture induced instability issues. After the anion exchange reaction is over, the CsPb(Br/I)₃ NCs could still be re-dispersed in toluene, which indicated that the NCs are still capped with the ligands (OA and OLA), also confirmed the presence of the ligands by proton nuclear magnetic resonance (¹H NMR) spectroscopic measurement of CsPbI₃ NC, re-dispersed in toluene-d₈ (denoted by *), shown in Figure 1A.^{28, 43} Though, the exchange takes place at the water-toluene interface, the surface of NCs remained unaffected by halide exchange process and the reaction conditions. It has been reported earlier that carboxylate ion (OA⁻) coordinates with the Pb²⁺ and oleylammonium ions binds with the halide ions on the surface.⁴³⁻⁴⁵ Reportedly, the overall ligand density is known to be significantly low in CsPbI₃.⁴⁶ In Figure 1, the alkene resonance for both OA and OLA can be seen

in the region $\delta = 5.6$ to 5.8 ppm. The resonance shifts upfield and broadened relative to neat OA and OLA ($\delta = 5.42$ ppm) indicated that the ligands are bound to the surface of the NCs.^{43, 47} Moreover, the decrease in intensity of the alkenyl region $\delta = 5.6$ to 5.8 ppm in CsPbI₃ NCs, signifies that the total ligand concentration decreased after halide exchange. Similar observations were also made in KBr passivated CsPbBr_xI_{3-x} NCs.¹⁵

Figure 1. ¹H NMR spectra of (A) halide exchanged CsPbI₃ NCs (B) FABr treated CsPbBr₃ NCs, dispersed in toluene-d₈ (denoted by *) and purified with methyl acetate (MeOAc).

Another concern was the possibility of FA⁺ ions to get exchanged with the Cs⁺ ions along with the halide ions. In order to rule out such a possibility, we have carried out a control experiment involving the addition of FABr to CsPbBr₃ NCs using the same protocol (refer to experimental

section for details). In case, if FA^+ ions replace Cs^+ ions, there would have been a red shift in emission due to lattice expansion (size of $\text{FA}^+ > \text{Cs}^+$). Similar, red shift upon incorporation of larger methylammonium cation ($\text{MA}^+ > \text{Cs}^+$) was earlier reported by Akkerman et al.³¹ As expected, the NCs obtained from this control reaction didn't show any change in the emission position and PL lifetime (shown in Figure S1, SI), indicating that Cs^+ ions remain intact in the crystal lattice during the halide exchange process. Further, we recorded ^1H NMR spectrum of the FABr treated CsPbBr_3 re-dispersed in toluene- d_8 , shown in Fig 1B. Both the ^1H NMR spectra (Figure 1A and 1B) showed no signature of FA^+ , which otherwise shows resonance in the region 7.78-7.88 ppm.^{48, 49} Thus, it was confirmed that there was no exchange of FA^+ ions with the Cs^+ ions in the perovskite lattice.

Figure 2A shows the PL spectra of CsPbBr_3 NCs, before and after treatment with FAI salt in water. The CsPbBr_3 NCs re-dispersed in toluene showed an emission peak at 510 nm with PLQY of 68.6%. We used three different concentrations (0.024 mM, 0.044 mM, and 0.058 mM) of FAI, to carry out the anion-exchange and tune the emission colour consecutively (refer to the experimental section). Due to the fair solubility of FAI in water, the reaction completes in less than a minute, with the maximum replacement reaction of Br^- with I^- limited to the amount of available I^- ions in the aqueous media. It is worth to mention that this new method does not require excess halide precursors to facilitate the halide exchange process; whereas most of the conventional methods require 10-20 fold excess of halide precursors^{31, 32} which could potentially destabilize the system.^{21, 36} We found that upon addition of 0.024 mM of FAI to CsPbBr_3 NCs, the emission peak position is shifted from 510 nm to 620 nm, forming $\text{CsPbBr}_{3-x}\text{I}_x$ NCs, with a concomitant increase in PLQY up to 94.2%. The time-resolved PL dynamics (Figure S2, SI) shows that the effective lifetime of the NCs increases from ~6.0 ns to ~18 ns with the incorporation of iodides, which is in accordance with the literature.⁷ Further increase of the FAI concentration yields a more complete

substitution with shown by the further redshift of the PL peak. The full width at half maximum (FWHM) of emission is calculated to be 20 nm for CsPbBr₃ NCs and which remained consistent with all the iodide substituted compositions, indicating the narrow size distribution in NCs.⁵⁰ The halide exchanged CsPbBr₃I_{3-y} NCs (PLQY~87%) and CsPbI₃ NCs (PLQY~74.1%) have emission at 630 nm and 660 nm, respectively. From the absorption spectra in Figure 2A, we determine the bandgap (E_g) of the CsPbBr₃ and CsPbI₃ NCs (from complete halide substitution) to be 2.43 eV and 1.87 eV, respectively.

Figure 2. (A) Photoluminescence (excitation at 400 nm) and UV-visible spectra (inset: image of NCs under visible light), (B) powder XRD patterns and (C) TEM images (scale bar= 20 nm) with high-resolution TEM in insets (scale bar= 5 nm) of (a) pristine CsPbBr₃ NCs and those after iodide exchange (b) CsPbBr_{3-x}I_x NCs (c) CsPbBr_{3-y}I_{3-y} NCs and (d) CsPbI₃ NCs.

For the stability test of the NCs, we monitored the PL emission of our halide exchanged NCs deposited as thin films, up to 15 days under ambient conditions (Figure S3, SI). The PLQY of $\text{CsPbBr}_{3-x}\text{I}_x$ NCs deposited as thin film, decreased from 49% to 36% with a shift in emission from 629 to 615 nm, whereas, the PLQY of $\text{CsPbBr}_y\text{I}_{3-y}$ NCs films decreased from 43% to 27% with 6 nm blue shift in emission (from 639 nm to 633 nm). Such blue-shifts are reportedly due to the effect of light and moisture on perovskite crystal lattice.⁵¹ Interestingly, the pure CsPbI_3 NCs are found to be more stable than the iodide-bromide mixed NCs with a minimum blue shift of 3 nm (from 667 nm to 663 nm) and drop in PLQY from 32% to 15%, after 15 days of deposition on thin film.

The phase purity of the halide exchanged NCs were confirmed from their powder XRD patterns (Figure 2B). A shift towards a lower 2-theta angle (as compared to the pristine CsPbBr_3 NCs) was observed in the NCs with increasing concentration of iodide. This is expected due to the change in lattice parameters associated with the replacement of smaller Br^- ions with bigger I^- ions.^{20,34} The average particle size of the NCs is estimated to be in the range of 8-10 nm from transmission electronic microscopic (TEM) images and no significant change in the average size was observed after halide exchange (Figure 2C). High-resolution TEM images of the NCs are shown in the insets of Figure 2C. A lattice spacing of 0.58 nm and 0.62 nm was observed in the CsPbBr_3 and CsPbI_3 NCs, respectively, which corroborate with literature reports.⁷ We have also compared the optical and structural properties of our halide exchanged CsPbI_3 NCs with those of CsPbI_3 NCs synthesized directly through the hot-injection method (refer to experimental section for the synthesis method). The freshly prepared directly synthesized CsPbI_3 NCs re-dispersed in toluene have PLQY ~ 37%. The halide exchanged $\text{CsPb}(\text{Br/I})_3$ NCs remained stable for months in solution with only slight precipitation. Absorption spectra are shown in Figure S4, SI for

CsPb(Br/I)₃ NCs stored in ambient conditions for a period of 65 days. However, the directly synthesized CsPbI₃ NCs agglomerates and quickly degraded the following washing with anti-solvent. We recorded powder XRD patterns of halide exchanged CsPbI₃ NCs after 1.5 months of halide exchange (Figure S5A, SI). During this incubation period, the exchanged NCs re-dispersed in toluene were stored under ambient condition before drop casting on thin film for powder XRD measurements. Powder XRD measurement were also done for CsPbI₃ NCs directly synthesized by hot injection, which were deposited on thin film within 2 hours of synthesis, followed by washing with anti-solvent (Figure S5B, SI). Unlike, those of halide exchanged NCs, we found that directly synthesized CsPbI₃ NCs showed several extra impurity peaks (shown in Figure S5B, SI) which corresponds to the orthorhombic CsPbI₃ and CsI.²¹ Further, absorption (shown in inset) and PL emission spectra (in Figure S6A) of the NCs obtained from direct synthesis showed a redshift of 10 nm (from 665 nm to 674 nm) with significantly reduced intensity upon washing with acetonitrile. The gradual degradation of the washed CsPbI₃ NCs are shown in the digital images of the NCs (Figure S6B). On the other hand, in case of halide exchanged CsPbI₃ NCs, the PL intensity reduces slightly after washing with anti-solvent without any shift in peak position (Figure S7, SI).

Note that post-synthetic halide exchange method has the advantage that prior to halide exchange, the pristine CsPbBr₃ NCs could be washed a few times, which is not possible with CsPbI₃ NCs. We also fabricated LED devices using directly (hot-injection method) synthesized CsPb(Br/I)₃ and CsPbI₃ NCs, as emitter layer, results shown in Figure S8, SI. We found that LED devices based on- CsPb(Br/I)₃ and CsPbI₃ NCs exhibited peak external quantum efficiency (EQE) of 0.3% and 0.47% with luminance turn-on voltage at ~ 3.7 V and 4.2 V, indicated presence of excess ligands on the surface of these NCs.

To check versatility of our halide exchange method, we wanted to investigate if the method also works well with similar other perovskite precursors. We used methyl ammonium iodide (MAI) and tetrabutyl ammonium iodide (TBAI) as iodide precursors. The details are presented in the experimental section. Upon addition of 0.012 mM and 0.024 mM of TBAI along with water to the CsPbBr₃ NCs in toluene (toluene: water ~ 2:1) showed emission at 560 nm and 578 nm, respectively (Figure S9, SI). Similarly, upon addition of 0.024 mM, 0.044 mM and 0.058 mM of MAI along with water to the CsPbBr₃ NCs, the emission maxima shifted from 512 nm to 636 nm, 667 nm, and 674 nm, respectively (Figure S10, SI). We also used tetrabutylammonium chloride (TBA-Cl) to check if the protocol works for bromide to chloride ion exchange too. Surprisingly, we have observed cyan colours at 476 nm and 484 nm when pristine CsPbBr₃ NCs were treated with 0.024 mM and 0.035 mM of TBA-Cl, respectively (Figure S11, SI). However, the colloidal, as well as phase stability of the NCs obtained from these halide sources (TBAI and MAI), were found to be poor compared to the NCs obtained from FAI as the iodide precursor. Consequently, we continued our studies with NCs, where FAI salt was used as iodide precursor. All the optical measurements and results (except Figure S9, S10 and S11) presented here are from such FAI treated NCs.

Given the high PLQY and the high color purity, we have fabricated LEDs with the synthesized iodide and iodide/bromide based NCs, as emitter layer (refer to experimental section, for the fabrication and characterization details). The device architecture consists of ITO/PEDOT:PSS/CsPb(Br/I)₃ NCs/POT2T/Al/Ca, where PEDOT:PSS acts as the hole-injection layer and POT2T acts as electron-transport layer. The current density-voltage-luminance of the fabricated devices (Figure 3A) reveals that the devices have ideal diodes characteristics with Ohmic linear behavior at low voltages and sharp diode current turn-on around 1.7 V. Figure 3A

also shows luminance–voltage (L–V) curves of the devices with a sharp luminescence turn-on voltage at around 2.4 - 2.6 V. The maximum value of luminance was calculated to be 580, 800 and 114 cd m^{-2} for our $\text{CsPbBr}_{3-x}\text{I}_x$, $\text{CsPbBr}_y\text{I}_{3-y}$ and CsPbI_3 –based devices, respectively. As shown in Figure 3B, the EQE of these LEDs increased sharply as soon as the devices were turned-on and decreased as the current density increased. These devices reached a maximum EQE of 0.47%, 0.49%, and 1.86% when halide exchanged $\text{CsPbBr}_{3-x}\text{I}_x$ NCs, $\text{CsPbBr}_y\text{I}_{3-y}$ NCs and CsPbI_3 NCs, respectively were used as emitter layer. Thus, the LED performance of halide exchanged NCs, in terms of low luminance turn-on voltage, brightness and EQE, was much better when compared to directly synthesized $\text{CsPb}(\text{Br/I})_3$ and CsPbI_3 NCs (shown Figure S8, SI). It must be mentioned that, the decrease in EQE at high current density operation, also known efficiency droop, has been previously observed and attributed to the thermal degradation of the materials when driven at a large current density.⁵² The exact mechanism of the efficiency droop in perovskite LEDs has not been completely understood yet. The possible causes include heat degradation,⁵³ enhanced Auger recombination,⁵⁴ carrier overflow at high carrier population,⁵⁵⁻⁵⁷ and a carrier delocalization effect⁵⁸. Such a phenomenon is also commonly observed in the nitride-based LEDs. The electroluminescence (EL) spectra (Figure 3C) collected at the maximum luminescence are centred at 629 nm, 643 nm and 670 nm for LED devices based on $\text{CsPbBr}_{3-x}\text{I}_x$ NCs, $\text{CsPbBr}_y\text{I}_{3-y}$ NCs and CsPbI_3 NCs, respectively and has full-width-at-half-maximum (FWHM) in the range of 33-43 nm. The EL spectra are slightly red shifted when compared to their respective PL spectra (Figure 2A) of NCs in solution.

Figure 3. Characteristics of LED devices using (a) $\text{CsPbBr}_{3-x}\text{I}_x$ NCs, (b) $\text{CsPbBr}_y\text{I}_{3-y}$ NCs and (c) CsPbI_3 NCs. (A) Current density – voltage – luminance characteristics of fabricated LEDs. The inset summarizes the maximum luminance and the turn-on voltage (at 1 cd m^{-2}) of the devices. (B) The external quantum efficiency (EQE) as a function of current density. The inset shows the device structure of LEDs. (C) The electroluminescence spectra at maximum luminance. The inset summarizes the peak position and the full-width-at-half-maximum (FWHM) of the EL spectra.

We also recorded the current density-voltage and radiance-voltage curves, which are shown in Figure 4A. The maximum value of radiance achieved was 7.8, 13.0 and 3.0 W sr⁻¹ m⁻² (Figure 4A) for CsPbBr_{3-x}I_x, CsPbBr_yI_{3-y} and CsPbI₃ -based devices, respectively. EL spectra were also collected at the maximum radiance, shown in Figure 4B. To check the EL spectral stability of these iodide containing NCs, we measured the EL spectra with increase in driving voltage. Gaussian fitting analysis showed that the EL peaks are red-shifted (Figure 4C) and broadened with increasing driving voltages (Figure 4D). We observed that the red shift and broadening are more distinct in NCs with a lesser amount of iodide content, i.e. CsPbBr_{3-x}I_x, the EL peak started to red shift at driving voltage of 4.2 V from 632 nm to 675 nm at 8 V. While the EL peak of the device based on CsPbI₃ NCs remained nearly at 670 nm up to driving voltage of 6 V, beyond that there is slight red shift in the peak position to 675 nm. For CsPbI₃ NCs based LED device, the FWHM was much narrower (~29 nm), however FWHM slowly increases to 42 nm at increasing driving voltage 6 V to 8 V.

Figure 4. LED characteristics and color emission stability of (a) $\text{CsPbBr}_{3-x}\text{I}_x$ NCs (b) $\text{CsPbBr}_y\text{I}_{3-y}$ NCs and (c) CsPbI_3 NCs, where FAI salt was used for ion-exchange. (A) Current density – voltage – radiance characteristics of fabricated LEDs. The inset summarizes the maximum radiance and the turn on voltage of LEDs, (B) the electroluminescence spectra collected at maximum radiance. The corresponding peak and FWHM are summarized in the inset. The peak positions (C) and FWHM (D) of electroluminescence spectra, as a function of the operating voltages of the LEDs. The values are obtained by fitting the spectra with a single Gaussian peak equation. The error bars are the errors from the Gaussian fitting.

We attributed this red shift of EL peak maximum to the phase segregation of the mixed halide NCs, driven under high electric field.¹² While, it is an undesired characteristic for LED display and lighting application, the change in emission color changed under the electric field can be potentially used for constructing color-switching memory devices, if reversibility could be achieved. Voltage-controllable multicolor emission has been previously demonstrated with lead halide perovskite and quantum dots emitters.⁵⁹

CONCLUSIONS

In summary, we have demonstrated a facile and green protocol for the halide exchange in CsPbBr₃ NCs using an aqueous-organic solvent system. The reaction is fast and generic in nature and requires only few seconds to complete. The halide exchanged NCs in cubic phase have high stability and PLQY, both in solution as well as in thin films. In addition, the protocol doesn't require excess halide precursors or other reagents and the final products are free from unwanted byproducts and impurities that are known to diminish the performance of these NCs in devices. We also demonstrated the application of these NCs as LED's active layer. The devices showed the luminescence turn-on voltage at around 2.4 - 2.6 V, which is relatively very low for the state-of-the-art of red-LEDs.^{11, 12} Our red emitting, CsPbBr_yI_{3-y} NCs showed the high luminance of 800 cd m⁻², while CsPbI₃ NCs with a luminance of 114 cd m⁻² showed EQE of 1.9%. Moreover, the pure CsPbI₃ NCs are found to be more resistant to phase segregation. The EL peak maximum at 670 nm and FWHM remained nearly same up to driving voltage of 6 V. More in-depth studies are required to establish the origin of the observed phase purity (selective cubic phase formation) in this halide exchange process while keeping OA and OLA as capping ligands.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge at <https://>

UV–visible absorption, Photoluminescence (PL) spectra; time-resolved PL spectra; time monitored PL spectra for stability check; power XRD patterns, digital images of the colloidal solutions of the NCs, LED device data for directly synthesized NCs (by hot-injection method).

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Notes

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