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Performance enhanced LEDs fabricated from nanocrystalline CsPbBr₃ with in-situ Zn²⁺ addition

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Abstract

Inorganic cesium lead halide perovskite nanocrystals are promising materials for optoelectronic applications as they exhibit high thermal stability alongside precise colour tunability and high colour purity; however, their optical properties are degraded by surface defects. This work demonstrates a room temperature synthesis of CsPbBr₃ nanocrystals facilitating *in-situ* surface passivation via the incorporation of Zn²⁺ cations. The facile incorporation ZnBr₂ into the precursor solution facilitates Zn²⁺ substitution into the nanocrystal surface/sub-surface layers to induce passivation of existing Pb²⁺ and Br⁻ vacancies and increase the photoluminescence quantum yield (PLQY) from ~48% to ~86%. The XPS and solid state ¹H MAS NMR techniques show that the

key modification is a reduction of the octylamine:oleic acid ratio leading to a near charge-neutral surface; this is accompanied by the appearance of larger nanosheets and nanowires observed by quantitative powder XRD and HR-TEM. The suitability of these perovskite nanocrystals for electrically-driven applications was confirmed by the fabrication of light emitting diodes (LEDs), which demonstrate that the *in situ* Zn^{2+} passivation strategy enhanced the external quantum efficiency (EQE) by ~60%.

Keywords: All-inorganic perovskite nanocrystals, in-situ surface passivation, light-emitting diodes, zero-dimensional perovskite, room-temperature synthesis, solid-state NMR

Introduction

Quantum confined semiconductor nanocrystals exhibit superior optical properties compared to their bulk counterparts. Confinement increases the exciton binding energy, thus enhancing the rate of radiative recombination that stimulates an increased photoluminescence quantum yield (PLQY).¹⁻⁵ Moreover, nanocrystals exhibit narrow luminescence linewidths whose wavelength can be controlled by the nanocrystal dimensions.⁶ Metal halide perovskite nanocrystals have emerged as promising candidates to replace the state-of-the-art CdSe/ZnS (core/shell) nanocrystals.⁷⁻¹⁰ In less than a decade, perovskite nanocrystals have shown tremendous improvements in optoelectronic applications such as solar cells,¹¹⁻¹⁶ light emitting diodes,¹⁷⁻¹⁸ and photodiodes.¹⁹ The two families of metal halide perovskite chemical analogues can be classified as: (a) organic-inorganic (FAPbX_3 and MAPbX_3 , $\text{X} = \text{Cl, Br, I}$) and (b) inorganic (APbX_3 , $\text{A} = \text{Cs, Rb}$; $\text{X} = \text{Cl, Br, I}$).^{10,20} Organic-inorganic metal halide (OMH) perovskite nanocrystals show near-unity PLQY and external quantum efficiency (EQE) up to 16% in LEDs.²¹⁻²² However, OMH perovskites suffer from poor thermal stability, which limits their device performance in solar cells

and LEDs.¹⁰ In contrast, pure inorganic perovskite, CsPbBr₃ nanocrystals, exhibit high thermal decomposition stability (>500°C) and are a viable option for optoelectronic applications.²³⁻²⁴

Protesescu *et al.*⁸ reported the first synthesis of monodisperse CsPbX₃ (X= Cl, Br, I) nanocrystals using a hot-injection route with emission across the visible spectrum (410 - 700 nm) by adjusting the halide mixture and particle size to induce room temperature PLQY up to 90%. Subsequent studies by Dutta *et al.*²⁵ have reported a similar synthesis of CsPbX₃ (X= Cl, Br, I) nanocrystals with a near unity PL quantum yield, but with a higher injection temperature and a separate halide source. Others have used hot-injection methods to prepare CsPbX₃ (X= Cl, Br, I) nanocrystals of precise morphology²⁶ to fabricate light-emitting diodes.^{18,27-30} However, these reaction routes have limited scalability due to their complexity, cost and need for rapid cooling to quench crystal growth. To circumvent these issues a room temperature method known as ligand-assisted re-precipitation (LARP) is often employed, where the perovskite precursor salts are dissolved in a polar solvent such as dimethylformamide (DMF) then injected into a large volume of a solvent in which they have much poorer solubility such as toluene. This induces rapid perovskite crystallisation that can be restricted to the nanoscale by suitable ligands dissolved in either precursor solution. However, this method has not been widely exploited for the synthesis of CsPbBr₃ due to the poor solubility of CsBr in DMF, such that the nanocrystal ink was dilute and colloiddally unstable for LED fabrication.^{9,23,31-33} Moreover, the poor solubility of CsBr promotes Cs vacancy formation on the perovskite surface.³³ This was overcome by Veldhuis *et al.*³⁴ using a 21-crown ether to improve CsBr solubility and yield a concentrated CsPbBr₃ nanocrystal ink permitting the successful fabrication of LEDs with an EQE of 2.6% that was significantly lower than for LEDs produced using CsPbBr₃ nanocrystals prepared by hot-injection.^{30,34}

While surface/sub-surface defects in CsPbBr₃ nanocrystals compromise PLQY and device efficiency, organic passivation reduces these effects.^{28,30,35-36} but at the cost of reducing thermal stability. Alternatively, inorganic passivation can preserve the thermal resistance of CsPbBr₃ while improving PLQY.³⁷ Elsewhere, CsPbBr₃ surfaces coated with zero-dimensional Cs₄PbBr₆³⁸⁻³⁹ proved of limited value due to the dilute nanocrystal ink.

Another passivation strategy is by additional metal cation doping/surface treatment.⁴⁰⁻⁴⁵ A generic method introducing divalent cations such as Cd²⁺, Zn²⁺, Sn²⁺ to CsPbBr₃ nanocrystals is via hot-injection.⁴¹ Moreover, the post synthetic cation exchange using Zn²⁺ was also explored in chalcogenide nanocrystal and FA doped CsPbBr₃ nanocrystal systems.⁴⁶⁻⁴⁸ However, in the perovskite system, the crystal chemical doping of perovskite is kinetically inhibited at room temperature, so metal cations instead reside on the nanocrystal surface/sub-surface.⁴⁰ Zu *et al.*⁴⁰ presented a post-synthetic surface treatment using ZnBr₂ and 1,3-adamantanedicarboxylic acid (ADA) to passivate the surface traps in perovskite nanocrystals and enhance PLQY. However, the viability of these nanocrystals in electrically driven LEDs requires investigation.⁴⁰⁻⁴¹ Post-synthetic surface treatment complicates processing and often results in a) excessive ligands in the nanocrystal suspension due to poor purification that impedes the electrical conduction or b) low solubility of nanocrystals in solvent.¹ Therefore, enhancement in PLQY without translation to devices will be insufficient to demonstrate optoelectronic applications.

In this work, a crown ether-enabled LARP achieved novel *in-situ* surface passivation of CsPbBr₃ nanocrystals, where ZnBr₂ introduced Zn²⁺ to near surface environments as confirmed by Rietveld refinement of powder XRD patterns, high-resolution transmission electron microscopy (HR-TEM) and solid-state NMR techniques. The efficacy of Zn²⁺/CsPbBr₃ passivation lead to significant improvements in nanocrystal optical properties that are suitable for

LED applications with an EQE improvement of ~60% achieved. Also explored were the photophysical properties and conduction characteristics governing the devices fabricated using these nanomaterials.

Results and Discussion

XRD and TEM: CsPbBr₃ nanocrystals were synthesized by the LARP method with and without *in-situ* Zn²⁺ surface passivation. In an *in-situ* technique, ZnBr₂ salt is dissolved in perovskite precursor solution, which is then used for the synthesis of Zn²⁺ surface passivated nanocrystals. It should be noted that, no post-surface treatment is required for these nanocrystals synthesis, which make the process extremely simple. Rietveld refined XRD patterns of CsPbBr₃ and Zn-CsPbBr₃ conform to orthorhombic (*Pnma* *a* = 8.2 Å, *b* = 11.7 Å, *c* = 8.2 Å) perovskite (Figure 1a, 1b, and Figure S1) and are consistent with TEM findings (Figure 2). The orthorhombic lattice was evident by peak splitting (Figure S2b) and presence of (201) as an allowed reflection (Figures S2c). XRD peaks are broadened due to nanocrystallinity according to the Scherrer equation.⁴⁹ Zn-CsPbBr₃ sample shows no significant shift in 2θ peak, indicating no obvious structural inclusion of Zn²⁺ in the bulk of CsPbBr₃ NCs.⁴² The Zn-CsPbBr₃ was polymorphic and contained ~30 wt% of cubic (*Pm3̄m* *a* = 5.8 Å) CsPbBr₃ along with orthorhombic CsPbBr₃ (Figure 1 b, Figure S2) and significantly lower *R*_{wp} and *R*_{exp} values (Table S1). Cubic structure of CsPbBr₃ is generally considered less conducting than an orthorhombic crystal structure of CsPbBr₃.⁵⁰

In addition to the CsPbBr₃ dimorphs, a proportion of zero-dimensional Cs₄PbBr₆ (*R*-3C *a* = 13.7 Å, *c* = 17.2 Å) was present in powders of both materials with a characteristic peak at 13.5° (Figure 1a and 1b and S7) but not detected in thin-films due to strong preferred orientation (Figure S1b). As other reports of Zn²⁺ doped CsPbX₃ synthesis have not shown the powder XRD pattern coexisting Cs₄PbBr₆ may have been overlooked.⁴⁰⁻⁴¹ The Zn-CsPbBr₃ sample showed higher

Cs_4PbBr_6 content (8.0%) compared to the CsPbBr_3 (6.8%) sample. It is noted that X-ray methods would be poorly sensitive to a thin surficial coating of Cs_4PbBr_6 (see solid-state NMR section for micro-level analysis). The bond dissociation energy between Zn-Br is 142 kJ/mol, which is much smaller than the 247 kJ/mol bond dissociation energy of Pb-Br.⁵¹ Smaller bond dissociation energy of ZnBr_2 makes the release of bromine much faster in the reaction medium. Additionally, due to common ion effect, presence of ZnBr_2 perturbs the solubility of PbBr_2 , which results in lead deficient and bromine rich Cs_4PbBr_6 phase.⁵²

Figure 1. Powder XRD patterns (red and green lines) of (a) CsPbBr_3 nanocrystals and (b) Zn-CsPbBr_3 nanocrystals with Rietveld structural refinement fits (blue lines) using TOPAS and residual maps of both graphs (gray), (c) Zn XPS spectra of CsPbBr_3 and Zn-CsPbBr_3 nanocrystals confirming the presence of Zn^{2+} on the surface of Zn-CsPbBr_3 nanocrystals, (d) thermogravimetric analysis (TGA) of both samples showing high thermal stability in nanocrystals. The observed weight loss upto 300 $^{\circ}\text{C}$ is due to octylamine and oleic acid ligands.

Figure 2. Transmission electron micrographs (TEMs) of (a), (b) CsPbBr_3 and (d), (e), (g) Zn-CsPbBr_3 nanocrystals along with high-resolution TEM of (c) CsPbBr_3 and (f) and (h) Zn-CsPbBr_3 showing the lattice spacing and inset Fast Fourier transform (FFT) of corresponding CsPbBr_3 crystals, and (i) HR-TEM of nanosheets depicting the lattice spacing of 4.1 Å with an inset of FFT corresponds to Cs_4PbBr_6 phase.

While Cs_4PbBr_6 is constructed from isolated $[\text{PbBr}_6]^{-4}$ octahedra separated by Cs^+ cations, the octahedra of CsPbBr_3 create a corner-connected 3D network.^{39,53} The latter enables electronic delocalisation such that excitons can easily dissociate and diffuse along the Pb-X-Pb bonds as a

free carriers.^{38,54} Conversely, the isolated octahedra exhibited by Cs_4PbBr_6 confining excitons within the octahedra, resulting in much higher exciton binding energy (353 meV) than in 3D CsPbBr_3 (50-60 meV).^{53,55}

Surface sensitive X-ray photoelectron (XPS) spectra of CsPbBr_3 and Zn-CsPbBr_3 yield a Zn 2p chemical shift corresponding to ZnBr_2 ,⁵⁶ which is consistent with Zn^{2+} peak from previous report of Zn treated CsPbBr_3 (Figure 1c).⁴⁰ The presence of Zn 2p peak on the surface of nanocrystals indicates that Zn^{2+} fills the high density lead vacancies. The overall Zn content was estimated by high voltage (20 keV) energy dispersive X-ray spectroscopy (EDXS) measurements where characteristic X-ray energies are better separated to confirm a Cs:Pb:Br:Zn ratio of 1.00 : 0.90 : 3.12 : 0.03 (see Table S2 and Figure S8). Figure S6 shows the Pb-4f and Br-3d XPS spectra of both samples, it was found that the binding energy peak is shifted towards higher energy (0.14 eV) in Zn-CsPbBr_3 samples indicating the stronger interaction of Pb-Br species in comparison to the Pb-Br interaction in pristine CsPbBr_3 sample. Additionally, a quantitative analysis of bromide on nanocrystals surface revealed a bromide rich surface of Zn-CsPbBr_3 nanocrystals (Figure S6e). Thermogravimetric analysis (TGA) for CsPbBr_3 and Zn-CsPbBr_3 found 10% weight loss below 300 °C is attributable to the decomposition of organic ligands (Figure 1d). Beyond 300°C, Zn-CsPbBr_3 and CsPbBr_3 maintain thermal decomposition stability to 600 °C demonstrating ZnBr_2 passivation does not compromise the inorganic metal halide perovskite (Figure 2d).

HR-TEM images of pristine CsPbBr_3 nanocrystals exhibit characteristic cubic morphology with an average edge of 12.9 ± 1.4 nm (Figure 2a and 2b and S3)⁷ not dissimilar to Zn-CsPbBr_3 nanocrystals of average diameter of 12.6 ± 1.6 nm (Figure 2d and 2e and S3). In addition to nanocubes, the Zn-CsPbBr_3 sample contained anisotropic morphologies,⁵⁷ including nanowires (aspect ratio ~11:1) and larger nanosheets. The anisotropic growth along (101) plane (Figure 2h)

can be attributed to the fact that ZnBr_2 provides an excess halide source and thus promotes the reaction kinetics in preferred direction, which may result in nanowires formation. However, a micro level analysis on reaction kinetics is still required. The nanocubes exhibit a lattice spacing (d) of 4.2 Å, which corresponds to the $(200)_{\text{ortho}}$ plane of the orthorhombic CsPbBr_3 crystal structure (Figure 2c and 2f). The nanowires show a lattice spacing of 5.8 Å, corresponding to the $(-101)_{\text{ortho}}$ crystal plane (Figure 2h). However, the cubic and orthorhombic lattice dimensions are not readily differentiated by TEM. In addition to XRD measurements, Cs_4PbBr_6 was reconfirmed by dark-field TEM imaging (Figure S3), where the Cs_4PbBr_6 clearly shows the lighter contrast due to the smaller average atomic number compared to CsPbBr_3 . Therefore, based on the unique diffraction pattern (FFT of Figure 2i) and darker diffraction contrast of Cs_4PbBr_6 crystal (Figure S3), nanosheets in Figure 2i could be assigned to Cs_4PbBr_6 phase with a lattice spacing of 4.1 Å corresponding to (121) crystal plane. Overall, in-situ addition of ZnBr_2 not only promotes the formation of some nanowires and nanosheets as a result of anisotropic growth but also results in excess zero-dimensional Cs_4PbBr_6 phase.

Solid State NMR: A multinuclear solid state ^{133}Cs , ^1H and ^{13}C MAS NMR approach has been implemented to identify the short-range speciation and structural features that define the CsPbBr_3 and Zn-CsPbBr_3 nanocrystal systems (Figures 3a – c). In contrast to the ^{133}Cs MAS NMR data for bulk CsPbBr_3 which is characterised by a single narrow resonance at δ 117 ppm and a long T_1 relaxation time of ~ 103 s (see Figures 3a and S4, and Table 1), the ^{133}Cs MAS NMR data from the CsPbBr_3 and Zn-CsPbBr_3 systems is more complex. The ~ 13 nm average size of the cubic CsPbBr_3 nanocrystals allows some representation of the surface and sub-surface Cs^+ cation species to be observed relative to the more abundant bulk Cs^+ species.⁵⁸ As observed in Figure 3a both nanocrystal systems are described by three ^{133}Cs resonances observed in the $\delta \sim 100 - 120$ ppm, δ

~108 - 115 ppm and δ ~100 - 105 ppm shift ranges which are assigned to Cs^+ cation positions in the bulk, sub-surface and surface regions of these nanocrystals, respectively. The discrete nature of these resonances and their relationship with these structural regions is supported by the increasing ^{133}Cs linewidths and decreasing ^{133}Cs T_1 s with increasing proximity to the nanocrystal surface (see Table 1 and Figures S4a and b). These characteristics are representative of the Cs^+ speciation recently reported in a comparative MAS NMR study of the CsPbBr_3 and triple cation $\text{Cs}_x(\text{MA}_{0.17}\text{FA}_{0.83})_{1-x}\text{PbBr}_3$ ($x = 0 - 0.15$) nanocrystal systems.⁵⁸ These partitioned regions experience increasing short-range disorder and structural strain associated with the cumulative loss of translational symmetry especially for Cs^+ positions closer to the particle surface. A similar trend was recently reported in ^{195}Pt and ^{105}Pd NMR studies of Pt and Pd metal nanoparticle systems.⁵⁹⁻

⁶¹ From a direct comparison of the ^{133}Cs MAS NMR data characterising the CsPbBr_3 and Zn-CsPbBr_3 nanocrystal systems in Figures 3a and S4, and Table 1, it is apparent that Zn^{2+} incorporation introduces minor differences, or no observable change, to most spectral features. The partial substitution of Zn^{2+} for Pb^{2+} in the PbBr framework induces a small upfield shift of ~2 ppm (i.e. to lower ppm) to the assigned surface resonance, and a slight upfield shift of ~1 ppm to the assigned sub-surface resonance. The corresponding resonance at 120 ppm representing the bulk region in the Zn-CsPbBr_3 nanocrystal system appears unperturbed by the $\text{Pb}^{2+}/\text{Zn}^{2+}$ substitution. These observations corroborate XPS that found slight surficial Zn^{2+} enrichment (Figure 1(c)). Furthermore, to within experimental error, this minor level of surface substitution has not influenced the ^{133}Cs T_1 relaxation times suggesting that little change to the Cs^+ cation mobility has been introduced.

Figure 3. Solid state (a) ^{133}Cs MAS NMR data ($\nu_r = 35$ kHz), (b) ^1H MAS NMR data ($\nu_r = 35$ kHz), and (c) ^{13}C CPMAS data ($\nu_r = 35$ kHz) acquired at 14.1 T from the CsPbBr_3 and Zn-CsPbBr_3 nanocrystal systems. The spinning sidebands in the ^{133}Cs MAS NMR data are marked by an asterisk.

Of particular note is the change to the octylamine:oleic acid ratio as determined by the ^{13}C CPMAS and quantitative ^1H MAS measurements (Figures 3b and c respectively) that confirm the presence of these passivation ligands on both the CsPbBr_3 and Zn-CsPbBr_3 nanocrystal surfaces. For the CsPbBr_3 samples an octylamine:oleic acid ratio of $\sim 1.3:1$ was in excellent agreement with a previously reported ^1H MAS NMR study on a similar system characterised by smaller average particle sizes of ~ 11 nm.⁵⁸ However, the Zn-CsPbBr_3 surface showed a reduction in the octylamine:oleic acid ratio to $\sim 1.1:1$. This small but significant decrease indicates that the Zn^{2+} (IR = $0.74 \text{ \AA}$ CN=VI) with a significantly smaller ionic radius in comparison to Pb^{2+} (IR = $1.19 \text{ \AA}$ CN=VI) is tenanted on the disordered vacancy sites on the CsPbBr_3 surface neutralised with two Br^- surface species.⁵⁸ Hence, the small extent of Zn^{2+} substitution on the CsPbBr_3 surface induces a near-neutral surface charge and a more passive surface environment, which fills the surface vacancies by Zn^{2+} and additional Br^- ions. The neutral surface environment balance out the incorporation of Zn^{2+} in the surface of nanocrystals. As a result, the Zn-CsPbBr_3 nanocrystals exhibit better surface passivation, which results in concomitant enhancement of the radiative channels and thus significant enhancement in the PLQY (Figure 4a) of Zn-CsPbBr_3 sample (from 49 % to 86%).

Table1. The ^{133}Cs chemical shift (δ), relative intensity, linewidth ($\Delta\nu$) and T_1 data that characterise the ^{133}Cs MAS NMR data from the CsPbBr_3 and Zn-CsPbBr_3 nanocrystal systems shown in Figure 3.

Species	Cs ⁺ Cation Position	$\delta^{133}\text{Cs}$ (± 1 ppm)	Relative Intensity (± 2 %)		Linewidth $\Delta\nu$ (± 10 Hz)	T_1 (s)
CsPbBr₃ bulk		115	100		890	103 ± 5
CsPbBr₃ nanocrystals	surface	108	24 ^a	21 ^b	1800	6 ± 2
	sub-surface	117	25 ^a	22 ^b	620	16 ± 2
	bulk	120	51 ^a	44 ^b	340	47 ± 4
	Mixed phase	175		3 ^b	2120	-
	Cs_4PbBr_6	235		9 ^b	320	48 ± 2
	CsPb_2Br_5	356		1 ^b	430	4 ± 2

Zn-CsPbBr₃ nanocrystals	surface	106	24 ^a	17 ^b	1570	4 ± 2
	sub-surface	116	26 ^a	19 ^b	670	12 ± 2
	bulk	120	50 ^a	36 ^b	350	52 ± 4
	Mixed phase	176		3 ^b	1910	-
	Cs ₄ PbBr ₆	235		22 ^b	320	36 ± 2
	CsPb ₂ Br ₅	356		3 ^b	400	5 ± 2

^a Relative intensity ratios calculated from within the surface, sub-surface and bulk CsPbBr₃ and Zn-CsPbBr₃ nanocrystal regions only.

^b Relative intensity ratios calculated from all Cs species present.

While anisotropic morphologies such as nanosheets appear, in addition to the familiar nanocubes, these emerging morphologies do not influence the comparative bulk:sub-surface:surface ratios characterising the CsPbBr₃ and Zn-CsPbBr₃ nanocrystal systems (Table 1). However, a prominent resonance at ~235 ppm (see Figure 3a) confirms the formation of a Cs₄PbBr₆ as a secondary phase that is more abundant in Zn²⁺ bearing materials as confirmed by the XRD and TEM studies. A small downfield resonance at 356 ppm also appears in both nanocrystal systems. This resonance has been reported in a ¹³³Cs MAS NMR study of Cs₄PbBr₆ powders, where it was assigned as the second Cs environment in the Cs₄PbBr₆ crystal structure constrained by a Cs site ratio of 1:3.⁵⁸ However, the relative intensities of the 356 and 235 ppm resonances in Table 1, do not corroborate this ratio and that the previously reported assignment is incorrect. Alternatively, the 356 ppm resonance is assigned to minor amounts of the 2D tetragonal CsPb₂Br₅ phase. In particular, the relative amount of Cs₄PbBr₆ in the CsPbBr₃ sample is ~2.4%, whereas it constitutes ~6.6% of the Zn-CsPbBr₃ sample. The ¹³³Cs MAS NMR data in Figure 3a also indicates an additional species identified by a broad resonance at ~172 ppm that is observed consistently in both nanocrystal systems; this has been recently attributed to small concentrations of surface Cs⁺ species that are directly coordinated to the octylamine and oleic acid passivating ligands.⁵⁸

Photophysical Properties: The absorption and PL spectra of pristine CsPbBr₃ and Zn-CsPbBr₃ nanocrystals are characterised by narrow green emission peaks (511-515 nm) that accord with earlier reports of CsPbBr₃ nanocrystals.^{34,58} Comparable CsPbBr₃ and Zn-CsPbBr₃ nanocrystals show emission at 515 and 511 nm and full width half maxima (FWHM) of 18 nm and 20 nm, respectively. The broader FWHM for Zn-CsPbBr₃ arises from the mixed morphology observed by TEM (Figure 2) while the 4 nm blue-shift can be attributed to the surface/sub-surface inclusion of Zn²⁺,⁴¹⁻⁴² an interpretation is consistent with XRD, XPS and ¹H MAS NMR. Surface passivation leads to extended radiative recombination pathways as time-resolved PL (TRPL) spectroscopy found charge carrier lifetimes increased from 7.26 ns to 9.31 ns (Figure 4b) with PLQY of CsPbBr₃ (48%) significantly improved in Zn-CsPbBr₃ (86%) nanocrystals. Cs₄PbBr₆ may augment PLQY; however, the absolute increase in the content of this phase from ~2.4 wt% to ~6.6 wt% in Zn-CsPbBr₃ compared to CsPbBr₃ nanocrystal negates this possibility. Moreover, several studies found Cs₄PbBr₆ emission originates substantially,^{38,58,62-63} but perhaps not entirely,⁶⁴⁻⁶⁵ from embedded CsPbBr₃ nanocrystals. While the emission mechanism of Cs₄PbBr₆ requires further examination this work establishes that the major contribution of improved PLQY is due to the Zn²⁺ surface passivation of the CsPbBr₃ nanocrystals. Moreover, the PLQY stability of Zn-CsPbBr₃ nanocrystal was found to be superior over time, when both samples were stored under similar ambient conditions. The PLQY of Zn-CsPbBr₃ NCs reduced only 19% over 28 days, whereas pristine CsPbBr₃ sample displayed a remarkable reduction of 51% in PLQY (Figure S5e). The improvement in the stability of PLQY can be attributed to the ZnBr₂ inorganic surface passivation.

Figure 4. Optical properties and device characteristic measured from CsPbBr₃ and Zn-CsPbBr₃ samples depicting (a) absorption and photoluminescence spectra of CsPbBr₃ and Zn-CsPbBr₃ nanocrystals, (b) time-resolved PL spectra of CsPbBr₃ and Zn-CsPbBr₃ nanocrystal thin-films showing a remarkable improvement in charge carrier lifetime of Zn-CsPbBr₃ nanocrystal sample, (c) a schematic device diagram with energy band diagram and device photograph at 2.50 V, (d) a plot of current density versus voltage and luminance vs voltage, (e) a plot of EQE versus current density, (f) a plot of current efficiency vs luminance, and (g) a plot of power efficiency versus luminance. All of the device metrics show significant improvement of 40% in Zn-CsPbBr₃ LEDs.

The significant improvement in PLQY motivated the deployment CsPbBr₃ and Zn-CsPbBr₃ nanocrystals in LEDs using the device architecture presented in Figure 4c and the possible impact of insulating and zero-dimensional Cs₄PbBr₆ on device performance. The LED is composed of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS, 40 nm) / poly(4-butylphenyl-diphenyl-amine) (Poly-TPD, 30 nm) / nanocrystals (45 nm) / 2,4,6-tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine (POT2T, 45 nm) / LiF (0.8 nm) / Al (80 nm), respectively. PEDOT:PSS and Pol-TPD were hole transport and injection layers, respectively, whereas POT2T was the electron injecting layer (see Experimental section). Band diagram energies are literature values (Figure 4c).²⁷ Both devices exhibit bright green electroluminescence (EL) in the device photograph (Figure 4c) and EL spectra (Figure S5a). The EL energies of the devices fabricated from CsPbBr₃ and Zn-CsPbBr₃ nanocrystals exhibit narrow emission at 23 nm and 24 nm matching with their corresponding PL spectra (Figure S5a). More importantly, no EL peak shift was invoked by varying device input voltage (Figure S5b) and the J-V curve exhibits standard diode behaviour, with leakage current on the order of 10⁻⁴ mA cm⁻² (Figure 4c). The turn on voltage (V_t) of CsPbBr₃ and Zn-CsPbBr₃ nanocrystal-LEDs are estimated from the J-V-L curve as 2.50 V and 2.33 V (Figure 4d). A slight improvement in V_t can be attributed to the reduction in non-radiative recombination centres in Zn-CsPbBr₃ nanocrystal LEDs. A marginal reduction in the current density of Zn-CsPbBr₃ devices was observed, thought to be due to the larger band gap (more insulating) Cs₄PbBr₆ (See XRD in Figure 1) and less conducting cubic CsPbBr₃. However, this effect should be slightly mitigated by the formation of larger nanorods in Zn-CsPbBr₃ nanocrystals (Figure 2d, g, h, and i) that have longer intra-crystal diffusion pathways and fewer routes that lowers average resistivity;²⁶ additional micro-level electrical analyses are required to fully understand the detailed conduction properties of both samples. Figures 4e, 4f, and 4g show the relationship between EQE (%) vs current density (mA

cm⁻²), current efficiency (cd A⁻¹) vs luminance (cd m⁻²), and power efficiency (lm W⁻¹) vs luminance (cd m⁻²), respectively. For both LEDs, efficiency roll-off at higher current density was observed, similar to other reported perovskite LEDs (see Figure 4e). However, Zn-CsPbBr₃ devices showed a significant overall improvement in device metrics (see Figures 4 and S4). CsPbBr₃ nanocrystals LEDs show relatively higher luminance (3226 cd m⁻²) than Zn-CsPbBr₃ LEDs (1636 cd m⁻²), this could be attributed to the elimination of less conducting cubic CsPbBr₃ emitting species in pristine sample.⁵⁰ However, due to larger non-radiative component A₁ (extracted from bi-exponential fitting of TRPL data, see Table S4) and lower value of charge carrier lifetime (Figure 4b and Table S4), the Zn-CsPbBr₃ nanocrystals contain less defects/vacancies, which results in low leakage current and therefore higher current efficiency and EQE value in devices.⁶⁶ It should be noted that the crystals defects/vacancies may lead to high leakage current in LEDs.⁶⁶ CsPbBr₃ nanocrystal LEDs exhibit a maximum EQE (current efficiency) of 2.41% (6.81 cd A⁻¹) whereas Zn-CsPbBr₃ had a much higher EQE (current efficiency) of 3.87 % (11.32 cd A⁻¹). Additionally, CsPbBr₃ and Zn-CsPbBr₃ nanocrystals show luminous power efficiency of 7.62 at 20.87 cd m⁻² of luminance and 13.31 lm W⁻¹ at 4.26 cd m⁻² of luminance, respectively. The trend in power efficiency is consistent with EQE values and a significant improvement was observed in LEDs using Zn-CsPbBr₃ nanocrystals as an active material. Critical device statistics values are presented in Table 2, and the stability of the luminance of these devices under constant current was also measured (see Figure S5d). The Zn-CsPbBr₃ nanocrystal-LEDs exhibited up to a six fold higher operational stability, which is a further benefit of the enhanced surface passivation of CsPbBr₃ nanocrystals by the proposed Zn²⁺ passivation strategy.

Table 2. The device statistics for all fabricated LEDs. The maximum and average values are given for each device.

Sample Name	PLQY (%)	No. of Devices	Turn on Voltage [V _d]	Peak Luminance [cd m ⁻²]	Current Efficiency [cd A ⁻¹]	Luminous Power Efficiency [lm W ⁻¹]	EQE [%]
CsPbBr₃ nanocrystals	48 ± 4	8	2.50 [2.42 ± 0.09]	3226 [3150 ± 205]	6.81 [6.65 ± 1.51]	7.62 [7.14 ± 1.10]	2.41 [2.33 ± 0.65]
Zn-CsPbBr₃ nanocrystals	86 ± 6	8	2.33 [2.33 ± 0.02]	1636 [1579 ± 126]	11.32 [10.48 ± 1.40]	13.31 [12.38 ± 0.80]	3.87 [3.43 ± 0.50]

Conclusion

This research demonstrates that *in-situ* room temperature ligand-assisted re-precipitation (LARP) can passivate CsPbBr₃ nanocrystal surfaces with Zn²⁺ while maintaining higher concentration NC ink for LED fabrication. The HR-TEM, XRD, XPS and solid state NMR techniques detected the addition of ZnBr₂ to be crucial in, (a) driving the formation of nanowire and nanosheet morphologies that coexist with the expected CsPbBr₃ nanocubes, (b) promoting the formation of zero-dimensional Cs₄PbBr₆; and (c) passivating the Zn-CsPbBr₃ surface by inclusion of Zn²⁺ cations within the surfaces/sub-surfaces defects of these nanocrystals. The passivated Zn-CsPbBr₃ nanocrystals deliver markedly improved optical properties where PLQY increased from 48% to 86%. LEDs fabricated from Zn-CsPbBr₃ nanocrystals in LED devices improved EQE from 2.41% to 3.87% compared non-passivated materials. The flexibility and adaptability of this strategy would be equally appropriate to chloride, iodide and mixed halide perovskite nanocrystals.

Experimental

Materials. CsBr (99.999% trace metal basis, Aldrich), PbBr₂ (99.999% trace metal basis, Aldrich), ZnBr₂ (99.999% trace metal basis, Aldrich), dibenzo-21-crown-7 ether (97%, Aldrich), hexane (anhydrous, 99.8%, Aldrich), toluene (anhydrous, 99.8%, Aldrich), hexane (anhydrous, 95%,

Aldrich), N,N-dimethylformamide (anhydrous, 99.8%, Aldrich), dimethyl sulfoxide (anhydrous, 99%, Aldrich) octylamine (99%, Aldrich), and oleic acid (technical grade, 90%, Aldrich).

Synthesis. A slightly modified LARP methodology synthesized pure CsPbBr₃ nanocrystals from 0.1 mmol CsBr and PbBr₂ mixed with 0.1 mmol of dibenzo-21-crown-[7] ether solution.^{34,58} This was dissolved in 1 mL of DMF inside a nitrogen-filled glove box. 150 μ l of as-prepared precursor solution was added dropwise to a 5 mL solution containing toluene, 21 μ l of octylamine and 473 μ l of oleic acid. The nanocrystal synthesis was performed outside the glovebox. For *in-situ* passivation, 0.030 mmol of ZnBr₂ was added to the 0.1 mmol mixture of CsBr, PbBr₂, and dibenzo-21-crown-[7] ether to prepare the precursor solution in 1 mL DMF.

Purification. For both samples, the products were centrifuged at 10,000 rpm for 12 min, the supernatant phase discarded and the precipitate re-dispersed in 200 μ l hexane followed by further centrifugation at 1,000 rpm for 12 min. The supernatant was further characterized and the NC ink used for device fabrication. The highest ink concentrations required 5 to 6 separate reactions that were merged during the washing process.

Fabrication of LEDs: Patterned ITO substrates (sheet resistance $\sim 8 \Omega\text{cm}^{-1}$) were cleaned using consecutive 20 min sonication cycles in Hellmanex (10% solution in deionized water), deionized water, acetone and isopropanol, followed by UV-ozone treatment for 15 min. PEDOT:PSS (Clevios Al4083) solution was filtered using 0.45 μ l PVDF filter before spin coating on a cleaned ITO substrate at 4000 rpm for 60 s. The substrates were annealed at 130 $^{\circ}\text{C}$ for 20 min then transferred to an argon-filled glove box for the remaining processes and annealed again at 140 $^{\circ}\text{C}$ for 15 min inside a glove-box. Poly-TPD (5 mg ml⁻¹) was spin coated at 4000 rpm for 60 s followed by annealing at 140 $^{\circ}\text{C}$ for 30 min. CsPbBr₃ and Zn-CsPbBr₃ nanocrystals (in hexane) were spin coated at 2000 rpm (acceleration = 200 rpm s⁻¹) for 60 s. A 45 nm layer of POT2T was thermally evaporated under 10⁻⁶ Torr vacuum and subsequently 0.8 nm LiF and 80 nm Al electrodes were

1
2
3 evaporated through a shadow mask. All LEDs were encapsulated using UV-curable epoxy resin
4
5 before removing from the glove box for electrical characterisation.
6
7

8 **Synthesis of Cs₄PbBr₆:** The Cs₄PbBr₆ was prepared using a published method,⁵³ in which 5 mmol
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10 of CsBr and PbBr₂ were dissolved in a 5 mL of DMSO and stirred for 12 h inside a nitrogen-filled
11
12 glove box. The solution was heated (120 °C) and aged (6 h) before centrifugal settling. The
13
14 precipitate was collected with a Buchner funnel, washed three times with 2 mL DMSO, and dried
15
16 at 100 °C under vacuum overnight.
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18
19

20 **Supporting Information:** Experimental for characterization techniques; remaining XRD analysis
21
22 TEM micrographs and histograms; ¹³³Cs T1 NMR data; remaining optical properties and device
23
24 efficiency data; XPS data; XRD of Cs₄PbBr₆; EDXS spectra; A table for fitting parameters of
25
26 Rietveld refinements; a table for ¹H MAS NMR data; A table showing carrier lifetime components
27
28 extracted from TRPL spectra.
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42 **Author Contribution**

43
44 PV designed the project and carried out experiment related to the materials synthesis, XRD,
45
46 steady-state optical properties, and device fabrication. SGM, AB, and AAMB have contributed to
47
48 the TRPL and PLQY measurements with their valuable discussion on the optical properties. TW
49
50 and YF have contributed to the powder XRD and SEM-EDXS analysis. JVH designed the solid
51
52 state NMR measurements and BEG and TJNH acquired the NMR data. PV, TJW, and JVH wrote
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manuscript. All authors have given valuable comments to improve the results and discussion, and agreed to the final version of the manuscript.

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