Highly Emissive Blue Quantum Dots with Superior Thermal Stability via In Situ Surface Reconstruction of Mixed CsPbBr$_3$–Cs$_4$PbBr$_6$ Nanocrystals

Hyeonjung Kim, Jong Hyun Park, Kangyong Kim, Dongryeol Lee, Myoung Hoon Song,* and Jongnam Park*

Although metal halide perovskites are candidate high-performance light-emitting diode (LED) materials, blue perovskite LEDs are problematic: mixed-halide materials are susceptible to phase segregation and bromide-based perovskite quantum dots (QDs) have low stability. Herein, a novel strategy for highly efficient, stable cesium lead bromide (CsPbBr$_3$) QDs via in situ surface reconstruction of CsPbBr$_3$–Cs$_4$PbBr$_6$ nanocrystals (NCs) is reported. By controlling precursor reactivity, the ratio of CsPbBr$_3$ to Cs$_4$PbBr$_6$ NCs is successfully modulated. A high photoluminescence quantum yield (PLQY) of $>90\%$ at 470 nm is obtained because octahedron CsPbBr$_3$ QD surface defects are removed by the Cs$_4$PbBr$_6$ NCs. The defect-engineered QDs exhibit high colloidal stability, retaining $>90\%$ of their initial PLQY after >120 days of ambient storage. Furthermore, thermal stability is demonstrated by a lack of heat-induced aggregation at 120 °C. Blue LEDs fabricated from CsPbBr$_3$ QDs with reconstructed surfaces exhibit a maximum external quantum efficiency of 4.65\% at 480 nm and excellent spectral stability.

1. Introduction

Metal halide perovskite materials have been recognized as promising candidates for next-generation color displays because their high photoluminescence quantum yields (PLQYs), narrow full widths at half maximum (FWHM), ease of bandgap tuning, and solution processability fulfill the ITU-R Recommendation BT.2020 (Rec. 2020) of the International Telecommunication Union (ITU).[1–3] Recently, significant progress has been achieved in the development of near-infrared, red, and green perovskite light-emitting diodes (LEDs), with external quantum efficiencies (EQEs) reaching over 20\%.[4–8] However, the efficiency of blue perovskite materials has lagged far behind, with EQEs of 12.3\% in the sky blue region (475–490 nm) and 8.8\% in the blue region (460–475 nm) having been reported.[9,10] Furthermore, Joule heating during LED operation is inevitable; thus, the development of perovskite materials with superior thermal stability, in which thermal quenching is minimized, is an important issue for the practical application of perovskite LEDs.

Several strategies for obtaining blue-emitting perovskites nanocrystals (NCs) are available. One method involves mixed halides that include both Br and Cl anions.[11–17] Although this is a convenient method for bandgap engineering, easy formation of Cl$^{-}$ vacancies poses a limitation as it results in a deep trap state within the bandgap.[18–20] These defect sites cause perovskite layer degradation and ion migration, resulting in phase segregation in response to the application of an electric field during device operation.[21,22] A second method is to use Br-based 2D perovskite nanoplatelets and take advantage of the exciton quantum confinement effect.[23–27] In inorganic cesium lead bromide (CsPbBr$_3$) nanoplatelets, the emission can be controlled according to the number of [PbBr$_6$]$^{4-}$ layers; however, strong exciton–phonon coupling and a randomly oriented distribution of nanoplatelets result in low-performance LEDs.[28] A third strategy for achieving blue-emitting perovskites NCs is to reduce the crystal size of a perovskite material such that it is within the quantum confinement regime.[9,25–32] CsPbBr$_3$ NCs with sizes in the quantum confinement regime (denoted by quantum dots, QDs) usually suffer from low PLQYs and stability because they are strongly affected by surface defects when the surface-to-volume ratio is high.[33] In particular, small-sized QDs are easily degraded and undergo aggregation because of their high surface energy, leading to broad emission spectra and poor spectral stability such...
that the emission color is susceptible to changing to green at high temperature. To overcome these approaches have been attempted, including amorphous CsPbBr\textsubscript{3} shelling\cite{31} the addition of excess Br using ZnBr\textsubscript{2} as the source\cite{29,32} Sb\textsuperscript{3+} doping\cite{32} and acid etching-driven ligand exchange\cite{34}. However, few studies have been conducted on the application of blue LEDs incorporating highly stable CsPbBr\textsubscript{3} QDs\cite{39,40}. A quite different approach involves CsPbBr\textsubscript{3} NCs being embedded in a Cs\textsubscript{4}PbBr\textsubscript{6} matrix with a crystal size of several hundred nanometers or more, resulting in improved PLQY and stability\cite{15,16,17,18,19,20,21,22,23,24}. However, the literature reports in this area have been focused only on green emission, and Cs\textsubscript{4}PbBr\textsubscript{6}/CsPbBr\textsubscript{3} embedded structures are not suitable for electro luminescent devices because a 0D Cs\textsubscript{4}PbBr\textsubscript{6} phase has a wide bandgap of 3.95 eV and is insulating\cite{39,40}.

In this article, we report a unique method to enhance the PLQY and stability of blue-emitting CsPbBr\textsubscript{3} QDs via simultaneous generation of mixed CsPbBr\textsubscript{3} QDs and Cs\textsubscript{4}PbBr\textsubscript{6} NCs. By controlling the reactivity of the precursors, the size of the CsPbBr\textsubscript{3} QDs was controlled. As a result, an emission wavelength of 470 nm with a high PLQY of 90% was achieved. We investigated the effects of the Cs\textsubscript{4}PbBr\textsubscript{6} NCs on the photophysical properties and thermal stability of the CsPbBr\textsubscript{3} QDs by observing changes in their morphology and optoelectronic properties. Octahedron defect sites on the surface of CsPbBr\textsubscript{3} QDs were etched by the Cs\textsubscript{4}PbBr\textsubscript{6} NCs, resulting in defect removal. This CsPbBr\textsubscript{3} QD surface reconstruction decreases the defect density and eliminates nonradiative recombination pathways, leading to high efficiency and stability for the CsPbBr\textsubscript{3} QDs. The mixed NC solution retained 90% of its initial PLQY value over 120 days of storage under ambient conditions, with little change in the emission peak position and FWHM. Thermally induced aggregation and fusion were suppressed during 60 min of heating at 120 °C. Spectrally stable and efficient blue LEDs, having an EQE of 4.65% at 480 nm, based on the mixed NCs were achieved.

**2. Results and Discussion**

**2.1. Preparation of In Situ Generated Blue-Emitting NCs**

We synthesized a mixed solution of CsPbBr\textsubscript{3} and Cs\textsubscript{4}PbBr\textsubscript{6} NCs by modifying a previously reported synthetic method (details provided in the Experimental Section)\cite{41}. In a typical synthesis, cesium carbonate (Cs\textsubscript{2}CO\textsubscript{3}), PbO, oleic acid (OA), and 1-octadecene (ODE) were added to a three-necked round-bottom flask, and metal oleate complexes were formed by heating at 120 °C. Oleylammonium bromide (OLAM-Br) was prepared separately by reacting oleylamine and hydrobromic acid (HBr), and then this was injected at low temperature under Ar into the metal oleate complexes. In this step, the reaction temperature and the Cs to Pb precursor ratio, as important factors for obtaining high-quality NCs with blue emission in the range of 460–480 nm, were carefully controlled. The CsPbBr\textsubscript{3} to Cs\textsubscript{4}PbBr\textsubscript{6} NC formation ratio was modulated by varying the Cs to Pb precursor feed ratio, as described in a previous report\cite{42}. When the amount of Pb precursor exceeded the amount of Cs precursor, the formation of CsPbBr\textsubscript{3} NCs in the orthorhombic phase was favored (Figure S1, Supporting Information). When the Cs and Pb precursor ratio was fixed at 1:1 and the reaction temperature was reduced, the growth of NCs was suppressed, and small CsPbBr\textsubscript{3} NCs and Cs\textsubscript{4}PbBr\textsubscript{6} NCs were simultaneously co-synthesized. The emission wavelength of the QDs was 470 nm, and a high PLQY of above 90% was achieved. This phenomenon occurred because the depletion of the Pb precursor was slower than that of the Cs precursor\cite{42,43}. At low temperature, the difference between the reactivities of the metal precursors was maximized, hence formation of Cs\textsubscript{4}PbBr\textsubscript{6} NCs was promoted and the size of the CsPbBr\textsubscript{3} NCs was reduced (Figure 1).

We investigated the dependence of the photophysical properties of the as-synthesized NCs on the reaction temperature in the range of 60–160 °C. These NCs exhibited two peaks in the UV–vis absorption spectra: the first excitonic peak, between 450 and 500 nm, and a sharp peak centered at 313 nm (Figure 2a). The absorption peak at 313 nm originated from optical transitions between localized states of the isolated [PbBr\textsubscript{6}]\textsuperscript{4−} octahedron of Cs\textsubscript{4}PbBr\textsubscript{6} NCs\cite{44–46}. X-ray powder diffraction (XRD) patterns of the NCs allowed us to confirm that the first exciton peak is related to the bandgap of the luminescent CsPbBr\textsubscript{3} NCs. As shown in Figure 2b, the sample of synthesized NCs included both orthorhombic CsPbBr\textsubscript{3} NCs and rhombohedral Cs\textsubscript{4}PbBr\textsubscript{6} NCs, and the Cs\textsubscript{4}PbBr\textsubscript{6}-to-CsPbBr\textsubscript{3} ratio increased as the reaction temperature decreased. This result is consistent with the increase in the intensity of the absorption peaks at 313 nm in the UV–vis spectra. As the reaction temperature decreased from 160 to 60 °C, the first exciton peak was blueshifted, and the emission peak center shifted from the green (504 nm) to the blue (470 nm) wavelength region (Figure 2c). Transmission electron microscopy (TEM) analysis also indicated that CsPbBr\textsubscript{3} and Cs\textsubscript{4}PbBr\textsubscript{6} NCs coexisted in the samples, and lowering the temperature reduced the overall size of the NCs (Figure 2d–g and Figure S2 (Supporting Information)). In addition, when the particle sizes (diameters) were measured by focusing on the luminescent CsPbBr\textsubscript{3} NCs, the average size and relative standard deviations decreased from 9.3 to 3.5 nm and from 38.1% to 9.0%, respectively, as the reaction temperature decreased from 160 to 60 °C, because of the slow crystal growth rate at low temperature (Figure 2h). Because the size of the CsPbBr\textsubscript{3} NCs synthesized at a temperature below 160 °C was smaller than the exciton Bohr radius (≈7 nm)\cite{47}, the blueshift in the emission peaks resulted from a quantum confinement effect, and the reduction in FWHM was due to the size distribution and defect density decrease. It should be noted that as the reaction temperature decreases, the PLQY increases from 57.7% to 90.1%, contrary to previously reported general trends of increasing crystallinity and PLQY with temperature (Figure 2i).

**2.2. Stability of In Situ Generated Perovskite NCs**

In order to analyze the stability of the in situ generated CsPbBr\textsubscript{3}–Cs\textsubscript{4}PbBr\textsubscript{6} NCs (denoted by ISNsCs), we synthesized small CsPbBr\textsubscript{3} QDs (denoted by C-QD\textsubscript{113}) as a control group using a conventional method based on hot injection of Cs-oleate at 90 °C with control of the OA and oleylamine (OLAM) ligands (details provided in the Figure S3 in the Supporting Information and the Experimental Section)\cite{48}. Conventional CsPbBr\textsubscript{3} QDs (denoted by C-QD\textsubscript{113}) were obtained by hot injection of Cs-oleate at 90 °C with control of the OA and OLAM ligands. In general, small CsPbBr\textsubscript{3} QDs have high surface energies and a large number
of defects, and hence they can be ripened easily, resulting in a photoluminescence (PL) redshift. Upon examining the colloidal stability of ISNCs that had been stored under an environment with relative humidity of 65% and room temperature of 25 °C, little change in emission peak and FWHM was observed over 120 days, and 90% of the initial PLQY was retained (Figure 3a). By contrast, the emission wavelength of the C-QD113 without Cs₄PbBr₆ rapidly redshifted, moving from 458 to 475 nm within 30 days, even at room temperature (Figure 3d). To compare in detail the thermal stability of the prepared QDs, they were dispersed in toluene and incubated for a period of time at 120 °C. The C-QD113 were easily ripened and fused together at high temperatures, and the emission gradually shifted to longer wavelengths, with a green emission at 500 nm observed after 60 min of incubation (Figure 3e). The XRD data showed that a nonluminescent CsPb₂Br₅ tetragonal phase was formed simultaneously (Figure 3f). In the case of the ISNCs, the intensity of the emission centered at ≈510 nm increased slightly with time during the annealing process, but there was no shift in the position of the emission peak maximum and the blue emission was maintained with a slight decrease in PL intensity (Figure 3b). Furthermore, other crystal structures such as CsPb₂Br₅ were not generated, and the diffraction patterns indicated that the crystallinity of the ISNCs was improved (Figure 3c). The XRD and TEM results for the CsPbBr₃ QD sample verified that the rhombohedral CsPb₂Br₅ phase was not present and that the sample consisted entirely of CsPbBr₃ QDs of 4.3 nm in size (Figure S6, Supporting Information).

After mixing the separated CsPbBr₃ QDs (denoted by S-QD113) and NC416 for 1 h at room temperature in a weight ratio of 1:0 to 1:5, changes in morphology and optical properties were observed in a nonpolar solvent (Figure 4). As the relative NC416 amount was increased, the absorption intensity at 313 nm increased, while the first exciton peaks of S-QD113 gradually decreased in intensity and were blueshifted (Figure 4a). The emission peaks were also shifted to shorter wavelength, and the PL intensity was concomitantly improved (Figure 4b and Figure S7 (Supporting Information)). In addition to the optical properties, changes in particle size and morphology were observed. In the 1:2 ratio mixed solution, the size of the S-QD113 decreased from 4.32 to 3.87 nm, while the NC416 size increased from 13.38 to 14.51 nm (Figure 4c and Figure S8 (Supporting Information)). The morphology of the NC416 transformed from hexagonal to truncated diamond and assembled into zigzag shapes (Figure S9, Supporting Information). The etching of S-QD113 and the variation in the NC416 shape are a result of the high surface energy of the small CsPbBr₃ QDs and Cs₄PbBr₆ NCs generated with the CsPbBr₃ QDs. To investigate the role of the Cs₄PbBr₆ NCs, we conducted a systematic study to monitor the differences in the optical properties, defect levels, and morphology of CsPbBr₃ QDs with different amounts of added Cs₄PbBr₆ NCs. For this purpose, nonluminescent pure Cs₄PbBr₆ NCs (denoted by NC416) with diameters of 13.6 nm were prepared separately via a previously reported method (Figure S5, Supporting Information).[49] CsPbBr₃ QDs were separated from a crude solution and then mixed with Cs₄PbBr₆ NCs in different weight ratios from 0 to 5 in a nonpolar solvent. The separation of the CsPbBr₃ QDs from the crude solution involved extraction via a size selection process using methyl acetate as an antisolvent; a clear emission spectrum peaking at 477 nm was observed for the separated CsPbBr₃ QDs. Because Cs₄PbBr₆ NCs and relatively large CsPbBr₃ QDs were removed during the separation process, the absorption peak at 313 nm disappeared, and the PL peak was slightly blueshifted. The XRD and TEM results for the CsPbBr₃ QD sample verified that the rhombohedral CsPb₂Br₅ phase was not present and that the sample consisted entirely of CsPbBr₃ QDs of 4.3 nm in size (Figure S6, Supporting Information).

2.3. Effects of Cs₄PbBr₆ NCs on CsPbBr₃ QDs Quality

We hypothesized that the cause of the high PLQY and good thermal stability of the ISNCs was related to the presence of the
Figure 2. Characterization of perovskite NCs depending on the reaction temperature. a) UV–vis absorption spectra, b) XRD patterns, and c) PL spectra of samples synthesized at 60, 80, 120, and 160 °C, respectively. The insets are photographs of perovskite NCs in nonpolar solvents acquired under 365 nm UV light illumination. TEM images of the samples synthesized at d) 60 °C, e) 80 °C, f) 120 °C, and g) 160 °C; the inset of (e) shows a high-resolution TEM image the of CsPbBr3 NCs prepared at 80 °C. h) Histograms illustrating the distributions of CsPbBr3 NC sizes for the samples prepared at different reaction temperatures. i) Variations in emission wavelength, PLQY, and FWHM of the as-synthesized products with reaction temperature.

the structural lability of perovskite as a function of its ligand environment. The CsPbBr3 phase was successfully converted into the Cs4PbBr6 phase and vice versa using excess OLAM and OA in a previous study. In our system, NC416 had a relative excess of the OLAM ligand, so small S-QD113 were easily etched and the NC416 size was increased (Figure S10, Supporting Information).

Time resolved photoluminescence (TRPL) measurements were performed to determine the effects of the PLQY enhancement along with NC etching on the optical spectroscopic characteristics (Figure 4d). Decay curves were used to analyze the excited state radiative relaxation dynamics. The S-QD113 decay curve was fitted to a biexponential function with a 3.89 ns average lifetime. When S-QD113 was mixed with NC416, the decay curve of the resultant mixture fitted a monoexponential function well, and the average lifetime was gradually increased to 5.25 ns. This increment in the average lifetime could be a result of various effects, such as energy transfer between S-QD113 and NC416, a S-QD113 size effect, and a reduction in trap-state density; hence, we decided to examine each of these possible causes in turn. First, Cs4PbBr6 NCs have a wider bandgap than CsPbBr3 NCs, so energy transfer is possible when the distance between the two materials is sufficiently close. Xuan et al. reported that the lifetime and PLQY were increased in a perovskite composite, in a study in which CsPbBr3 NCs were embedded in Cs4PbBr6 NCs. In addition, Chen et al. synthesized CsPbBr3-embedded Cs4PbBr6 and analyzed the effect of metal halide interlayer in determining their photoluminescence excitation (PLE) properties. To investigate the energy transfer, we acquired PLE and PL spectra of S-QD113.
and ISNCs for various the excitation wavelengths (Figure S11, Supporting Information). The S-QD 113 emission intensity gradually decreased as the excitation wavelength increased, in line with the trend observed for the PLE spectrum. The PLE spectrum of the ISNCs included a sharp drop centered at around 313 nm corresponding to the Cs 4 PbBr 6 NC absorption peak. These results demonstrate that the origin of the PL of the ISNCs can be attributed to band edge emission of the CsPbBr 3 QDs rather than energy transfer from the Cs 4 PbBr 6 NCs. In the latter case, the ISNC emission would have improved significantly before the Cs 4 PbBr 6 NC absorption region. Therefore, we excluded the energy transfer effect in ISNCs. Second, for perovskites, lifetimes tend to decrease as bandgaps widen. 152–55 Since S-QD 113 is in the strong quantum confinement regime, the lifetime is expected to decrease with the decrease in particle size. However, in our study, when NC 416 was mixed with S-QD 113, the size of the S-QD 113 particles decreased slightly because of surface etching. This result, indicating a longer lifetime for smaller NCs, was contrary to our expectation. Therefore, we conclude that surface passivation effects are likely to be the main reasons for the longer lifetime, as reported previously. 56–57 The CsPbBr 6 NCs might promote the elimination of defects and radiative recombination in the CsPbBr 3 QDs.

To investigate in detail the optical properties of the NCs, the temperature-dependent PL of the S-QD 113 and ISNC samples was measured (Figure S12, Supporting Information). The PL intensity of the S-QD 113 sample gradually decreased as the temperature increased, in agreement with previous reports. 58–60 In metal halide perovskites, because of the low exciton binding energy, excitons are dissociated into free charge carriers by thermal energy, promoting nonradiative decay. 60–62 However, the ISNCs displayed a constant PL intensity, for the entire temperature range from 20 to 300 K. As the exciton binding energies of NCs are highly dependent on the size of the NCs, 59,62 we expect that the exciton binding energy of the S-QD 113 (≈4.32 nm) and ISNC (≈4.33 nm) samples would be similar. Therefore, the constant ISNC PL intensity as a function of temperature suggests that nonradiative decay paths are substantially reduced by the presence of Cs 4 PbBr 6.

In addition, we induced an interaction between the S-QD 113 and NC 416 samples on the substrate to identify the effects of defect passivation in the solid state. First, half of the substrate was covered with Kapton tape (3M #5413) and then NC 416 was spin coated on the exposed part. Subsequently, the experiment proceeded in order with the removal of ligands with methyl acetate, peeling off the tape, and coating S-QD 113 over the entire substrate. As a result, half of the substrate was covered with only S-QD 113, and the other coated with a double layer, with S-QD 113 and NC 416 in contact at the layer interface (Figure S13, Supporting Information). For this as-prepared film, initially there was no difference in emission between the two regions (A and B); however, the PL intensity was greatly improved in the double layer (layer B) after 12 h (Figure 4e,f). Although the interaction was relatively slow in the solid state, the S-QD 113 defects were also passivated similar to the solution. We summarized the above-described mechanistic findings in a schematic illustration (Figure 4g). Surface reconstruction takes place at the interfaces between the CsPbBr 3 QDs and CsPbBr 6 NCs, and imperfect octahedrons on the CsPbBr 3 QD surfaces are reduced during the etching process. In this process, the CsPbBr 3 QD crystal size

Figure 3. Stability of in situ generated perovskite NCs. Variations in emission wavelength, PLQY, and FWHM of a) in situ generated CsPbBr 3–Cs 4 PbBr 6 NCs (ISNCs) and d) conventional CsPbBr 3 QDs (C-QD 113) with incubation time under ambient conditions (relative humidity: 65%, temperature: 25 °C). Emission stability of b) ISNCs and e) C-QD 113 in toluene at 120 °C; the insets show photographs of the respective NCs acquired under UV light illumination. XRD patterns of c) ISNCs and f) C-QD 113 after annealing in toluene at 120 °C for various periods of time.
Figure 4. Characterization of the interaction between CsPbBr$_3$ QDs and Cs$_4$PbBr$_6$ NCs. a) UV–vis absorption and b) PL spectra for various ratios of separately prepared CsPbBr$_3$ QDs (S-QD113) and Cs$_4$PbBr$_6$ NCs (NC416). c) NC size histograms before and after mixing S-QD113 and NC416 at a weight ratio of 1:2. d) PL decay curves of S-QD113 and mixed S-QD113 and NC416. e) Photographs acquired under UV light illumination of the as-prepared sample (left) and the sample after storage for 12 h under ambient conditions (right). f) PL spectra of film in part A and B of the sample slide after 0 and 12 h. Part A of the film was coated with S-QD113 only and part B was sequentially coated with NC416 and then S-QD113. g) Schematics of S-QD113 surfaces produced by mixing S-QD113 and NC416 in weight ratios from 1:0 to 1:2. Imperfect octahedrons on the S-QD113 surface were peeled off upon addition of NC416.

decreases, resulting in a blueshift of the emission wavelength, and the optical properties and colloidal stability are increased by the addition of Cs$_4$PbBr$_6$ NCs.

2.4. Fabrication and Characterization of Blue Perovskite LEDs

Encouraged by the high PLQY and stability of the IS-NCs, we constructed LEDs with glass/indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(p-styrene sulfonate) (PEDOT:PSS)/poly[9,9-diocetylfluorenyl-2,7-diyl]-co-(4,4′-(N-(4-sec-butylphenyl)diphenylamine)] (TFB)+ poly(9-vinylcarbazole) (PVK) (30 nm)/ISNCs (20 nm)/2,2′,2′′-(1,3,5-benzinetriyl)-tris(1-phenyl-1H-benzimidazole) (TPBi) (70 nm)/LiF (1 nm)/Al (100 nm) structures. The thickness of each layer was confirmed via the acquisition of cross-sectional scanning electron microscopy (SEM) images (Figure 5a). Energy band diagrams for the materials employed in the LEDs are shown in Figure 5b. Due to the low Cs$_4$PbBr$_6$ HOMO energy level (7.2 eV), a triple hole injection layer including a polymer with a deep work function was used for efficient hole injection. The device performance characteristics of the ISNCs LEDs are shown in Figure 5c–f and Table S1 (Supporting Information). The LEDs fabricated with ISNCs exhibited a maximum luminescence of 23 cd m$^{-2}$ and EQE of 4.65% at wavelength of 480 nm. Histogram of maximum EQEs of ISNCs LEDs are shown in Figure S14 (Supporting Information).
Figure 5. Blue perovskite LED device structure and performance characteristics. a) Cross-sectional SEM image of ISNCs LED. b) Energy band diagram of the materials employed in LEDs. c) Current density–voltage (J–V) curve and luminance–voltage (L–V) curve, d) luminous efficiency–current density (LE–J) curve, and e) EQE–current density (EQE–J) curve of ISNCs LEDs. f) EL spectra of ISNCs LEDs at various voltages.

One of the most important problems for blue-emitting metal halide perovskites is the spectral instability that results from halide segregation. LED emission spectra measured using various voltage bias values are shown in Figure 5e. Because the ISNCs exhibited blue emission at 480 nm without halide mixing, the ISNC LEDs exhibited stable electroluminescence (EL) emission spectra over the entire range of device operating voltages.

3. Conclusion

In summary, we demonstrated a novel synthetic method to simultaneously obtain ultrasmall CsPbBr$_3$ QDs and Cs$_4$PbBr$_6$ NCs by controlling the ratio of the Cs and Pb precursors as well as the reaction temperature. CsPbBr$_3$ QDs of 3.5 and 4.3 nm in size – smaller than the exciton Bohr radius – were synthesized at 60 and 80 °C, respectively. These QDs emitted blue light at 470 and 477 nm, respectively, with high PLQYs of more than 90%. The Cs$_4$PbBr$_6$ NCs eliminated the imperfect octahedron defect sites on the surfaces of the CsPbBr$_3$ QDs, which resulted in suppression of nonradiative recombination; this was confirmed via TRPL and temperature-dependent PL measurements. In addition, the colloidal and thermal stabilities of the ISNCs were significantly enhanced by suppressing particle aggregation and fusion. We realized efficient blue LEDs with a maximum EQE of 4.65% at 480 nm. In particular, the EL spectra were stable across various applied voltages, without exhibiting any peak shifts. This surface defect etching method, which relied on CsPbBr$_3$ and Cs$_4$PbBr$_6$ phase surface reconstruction, was found to be effective even for solid-state films. Thus, our strategy could expand the development of a wide range of perovskite optoelectronic applications.
including solar cells and NC-based LEDs, thanks to the introduction of a new method for controlling the amount of defects.

4. Experimental Section

Materials: OLAM (98%), HBr (48%), Cs₂CO₃ (99.9%), PbO (99.999%), ODE (90%), OA (90%), and lead bromide (PbBr₂, 98%) were purchased from Sigma-Aldrich. Acetonitrile (ACN, 99.5%), toluene (99.8%), methyl acetate (99.5%), and hexane (99.5%) were purchased from Samchun Chemicals. All the chemicals were used without further purification.

Preparation of OLAM-Br Precursor: The OLAM-Br salt was synthesized according to a previous method with some modifications. In a typical synthesis, OLAM (10 mL) and HBr solution (1.3 mL) were loaded into a 50 mL three-necked round-bottom flask, and the resulting solution was stirred under an Ar atmosphere at 120 °C for 2 h. Then, it was heated to 150 °C and left to react for an additional 30 min. After cooling the solution to 100 °C, it was vacuum dried for 1 h to remove any residual water. The precursor was collected in an Ar-filled vial and stored in a glove box for further use.

Preparation of CsPbBr₃–Cs₄PbBr₆ NCs: A mixed CsPbBr₃/Cs₄PbBr₆ NCs were prepeared via an OLAM-Br precursor hot-injection method. Typically, Cs₂CO₃ (32.6 mg, 0.1 mmol), PbO (44.6 mg, 0.2 mmol), OA (1.0 mL), and ODE (10 mL) were stirred in a 50 mL three-necked round-bottom flask and degassed under vacuum at 120 °C for 1 h. After complete solubilization of the reaction mixture, the mixture was filtered with Ar and heated (or cooled) to obtain the desired temperature (60–160 °C). Then, the preheated OLAM-Br solution (0.9 mL) was swiftly injected into the reaction mixture. The reaction was quenched in an ice water bath after 30 min.

Purification of Synthesized NCs: The crude solution was transferred to a 50 mL conical tube and ACN and toluene were then added to the solution in a volume ratio of 1:1 (crude mixture:ACN:toluene). The nanocrystals were precipitated in a centrifuge at 7000 rpm for 5 min. The supernatant was discarded, and the precipitate was collected and dissolved in hexane. One more centrifugation (7800 rpm, 5 min) was required to purify the NCs and obtain the final product. The clear supernatant was collected and used for future studies.

To eliminate the Cs₄PbBr₆ NCs from the crude solution, methyl acetate was used as an antisolvent instead of the mixture of ACN and toluene. Typically, methyl acetate (5 mL) was added to the crude solution (5 mL). This solution was centrifuged at 7800 rpm for 5 min and the precipitate was discarded. An additional methyl acetate (20 mL) was added to the supernatant, and this mixture was centrifuged at 7800 rpm for 5 min. The precipitated CsPbBr₃ QDs (S-QD113) were used in further studies after dispersion in hexane.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

blue quantum dots, light-emitting diodes, perovskites, surface reconstruction, thermal stability

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