Hollow Metal Halide Perovskite Nanocrystals with Efficient Blue Emissions

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Hollow Metal Halide Perovskite Nanocrystals with Efficient Blue Emissions

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Abstract

Metal halide perovskite nanocrystals (NCs) have emerged as a new generation light emitting materials with narrow emissions and high photoluminescence quantum efficiencies (PLQEs). Various types of perovskite NCs, e.g. platelets, wires, and cubes, have been discovered to exhibit tunable emissions across the whole visible spectral region. Despite remarkable advances in the field of metal halide perovskite NCs over the last few years, many nanostructures in inorganic NCs have yet been realized in metal halide perovskites and producing highly efficient blue emitting perovskite NCs remains challenging and of great interest. Here we report for the first time the discovery of highly efficient blue emitting cesium lead bromide perovskite (CsPbBr₃) NCs with hollow structures. By facile solution processing of cesium lead bromide perovskite precursor solution containing additional ethylenediammonium bromide and sodium bromide, in-situ formation of hollow CsPbBr₃ NCs with controlled particle and pore sizes is realized. Synthetic control of

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hollow nanostructures with quantum confinement effects results in color tuning of CsPbBr$_3$ NCs from green to blue with high PLQEs of up to 81 \%.

Introduction

Metal halide perovskite nanocrystals (NCs) have received great attention as an emerging class of light emitting materials for their narrow emissions, exceptional photoluminescence quantum efficiencies (PLQEs) and color tunability. $^{1, 2, 3, 4}$ Various approaches have recently been developed to achieve synthetic control of the composition, size, and shape of perovskite NCs to obtain emission colors covering the whole visible spectrum, from deep blue to near-infrared. $^{5, 6, 7, 8, 9, 10, 11, 12, 13, 14}$ For instance, by manipulating the quantum size effect, the emission of CsPbBr$_3$ NCs can be tuned from green for NCs with sizes larger than the exciton bohr radius (~7 nm), to deep blue for quantum dots, nanowires, and nanoplatelets with strong quantum confinement. $^{15, 16, 17, 18, 19}$ $^{20}$ Although highly efficient perovskite NCs can be synthesized using colloidal methods, preserving the high PLQEs during transfer of colloidal NCs to thin films for device integration has been challenging. $^3$ On the other hand, in-situ formation of highly efficient perovskite NCs is not trivial either, because of the limited control on particle size, monodispersity, and surface passivation. This is even more relevant in blue emitting perovskite NCs, which are generally in the size range of 4-6 nm for CsPbBr$_3$ and thus possess high surface area to volume ratios that readily lead to high surface defect density and low PLQEs.
Hollow NCs, nanostructured materials with pores, provide an additional degree of freedom to exploit the quantum size effect by controlling pore and grain sizes. Several classes of hollow NCs have previously been reported, e.g. metal chalcogenides, metal oxides, metal nanoparticles, with applications in catalysis and energy storage. To the best of our knowledge, hollow metal halide perovskite NCs have not yet been discovered. Here, we report a novel approach to achieving highly efficient blue emissions from CsPbBr$_3$ perovskite NCs by creating hollow nanostructures with controlled sizes. By spin casting a mixture solution containing cesium bromide (CsBr), lead bromide (PbBr$_2$), ethylenediammonium bromide ((H$_3$N(CH$_2$)$_2$NH$_3$)$_2$Br$_2$), and sodium bromide (NaBr), in-situ formation of hollow CsPbBr$_3$ perovskite NCs can be facilely achieved. It was found that the [NH$_3$(CH$_2$)$_2$NH$_3$]$^{2+}$ (EDA$_2^+$) cations act as both surface passivation ligands and A-site cations that lead to the formation of randomly oriented Pb$_2^+$ vacancies, and subsequently hollow nanostructures with the presence of Na$^+$ cations. By carefully controlling the EDABr$_2$ and NaBr content, size tuning of pore and grain radii of hollow CsPbBr$_3$ perovskite NCs was achieved, resulting in emission color tuning from green (525 nm) to blue (459 nm) with high PLQEs of up to 81% at 498 nm and 72% at 478 nm. Our work introduces a new nanostructure to the family of metal halide perovskites, showing once again their exceptional structural versatility. The hollow perovskite NCs with tunable optical and electronic properties may have potential applications in various optoelectronic applications, for instance, blue light-emitting diodes (LEDs).
Results

The schematic diagram of a one-step spin-casting process for the preparation of metal halide perovskite thin films is shown in Figure 1a. Briefly, metal halide perovskite precursors, CsBr and PbBr$_2$, mixed with EDABr$_2$ and NaBr at controlled ratios, were spun cast on glass substrates, followed by low temperature thermal annealing at around 100 °C (see Experimental Details in Methods). By fixing the concentration of NaBr to 3 mol % with respect to the perovskite precursors and varying the molar ratio of EDABr$_2$ to the perovskite precursors (from 0 to 1.2), uniform and smooth thin films were produced as evidenced by the atomic force microscopy (AFM) images shown in Supplementary figure 1 a-f. The thickness of these thin films was measured to be 42 ± 8 nm (Supplementary figure 2). The thin films were transparent under ambient light, but displayed green and blue emissions under UV irradiation, as shown in figure 1b. The photophysical properties of the thin films were investigated via UV-Vis absorption, steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectroscopy, as well as photoluminescence quantum efficiency (PLQE) measurements. As shown in figure 1c, the absorption onset and the photoluminescence emission peaks were steadily shifted to lower wavelengths with the increase of the EDABr$_2$ concentration, while keeping the NaBr content constant. This blue shift of emission spectra was also associated with a pronounced increase in the PL decay lifetimes, as illustrated in figure 1d and tabulated in Supplementary table 1, indicating the role of the EDA$^{2+}$ cations in surface defect passivation.$^{26}$ The defect passivation is further supported by PLQE measurements, where samples containing increasing amounts of EDABr$_2$
showed a steep increase in PLQE, with a peak PLQE of 72% for the sample with 1:1 ratio of EDABr₂ to the perovskite precursor, as depicted in figure 1e.

**Figure 2** | Processing and photophysical properties of CsPbBr₃ containing thin films with 3mol % of NaBr and various concentrations of EDABr₂. **a**, A schematic showing the one-step spin coating followed by low-temperature thermal annealing. **b**, Thin films with various concentrations of EDABr₂ under ambient light (top) and UV irradiation (bottom). **c**, Photoluminescence and absorption spectra of CsPbBr₃ containing thin films with EDABr₂ molar ratio varying from 0 to 1.2 of the perovskite precursors. **d**, Time resolved photoluminescence decay curves of CsPbBr₃ containing thin films with EDABr₂ molar ratio varying from 0 to 1.2 with respect to the perovskite precursors. **e**, PLQE and emission peak wavelength of CsPbBr₃ containing thin films with EDABr₂ molar ratio varying from 0 to 1.2 with respect to the perovskite precursors.

To better understand the effects of NaBr and EDABr₂ on the photophysical properties of perovskite thin films, we systemically adjusted the concentration of NaBr with and
without the presence of EDABr₂, and vice versa. Changing the content of NaBr within the precursor solution, while keeping the concentration of EDABr₂ constant (1:1 with respect to the perovskite precursors) also afforded emission color tuning, from 498 nm for the sample without NaBr to 459 nm for that containing 4 mol% of NaBr (Supplementary figure 3a). However, the PLQEs steadily declined with the increase of NaBr concentration (Supplementary table 2). Controlling the content of NaBr without the presence of EDABr₂, however, had little-to-no effect on the photoluminescence spectrum and efficiency (Supplementary figure 4a). These results suggested that NaBr did not play a passivation role in the thin films as EDA²⁺. By controlling the EDABr₂ content without the presence of NaBr, limited color tuning was achieved, with the blue shift saturating at around 498 nm (Supplementary figure 4b). To reveal the structure-property relationships and understand the roles of Na⁺ and EDA²⁺ cations in these systems, we investigated four representative samples in detail, whose compositions and photophysical properties are summarized in Table 1. The sample CsPbBr₃ was prepared from the solution containing perovskite precursors without the addition of NaBr and EDABr₂, the sample CsPbBr₃–Na was prepared from the solution containing perovskite precursors and 3 mol % NaBr, the sample EDA5 was prepared from the solution containing perovskite precursors and EDABr₂ at 1:1 ratio; the sample EDA5–Na was prepared from the solution containing perovskite precursors and EDABr₂ at 1:1 ratio as well as 3mol% NaBr.
Table 1 | Composition and photophysical properties of representative samples

| Sample        | Composition (CsPbBr$_3$: EDABr$_2$: NaBr) | $\lambda_{em}$ (nm) | FWHM (nm) | $\phi^*$ (%) | $\tau_{avg}$* (ns) |
|---------------|------------------------------------------|---------------------|-----------|-------------|------------------|
| CsPbBr$_3$    | 1 : 0 : 0                                 | 525                 | 23        | 0.5         | 14               |
| CsPbBr$_3$–Na | 1 : 0 : 0.03                              | 525                 | 23        | 0.5         | 18               |
| EDA5          | 1 : 1 : 0                                 | 498                 | 22        | 81.5        | 200              |
| EDA5–Na       | 1 : 1 : 0.03                              | 478                 | 24        | 72          | 150              |

$^*\lambda_{em}$ is the wavelength at the emission maxima, $\phi$ is the PLQE; $\tau_{avg}$ is the average PL lifetime.

The structural properties of the four samples were investigated by selected area electron diffraction (SAED) and x-ray powder diffraction (XRD), as shown in figures 2a, b. The sample CsPbBr$_3$ was identified to have an orthorhombic phase (space group Pnma) and the diffraction peaks were indexed accordingly. Apart from small shifts, the other three samples displayed the same diffraction peaks without any sign of low-dimensional or non-perovskite phases, indicating the formation of a 3D perovskite structure. The shifts of the diffraction peaks are due to unit cell contraction or expansion. For the sample CsPbBr$_3$–Na, slight shifts to higher diffraction angles were observed ($\Delta2\theta \approx 0.022^\circ$ for the (121) plane and $\approx 0.054^\circ$ for the (202) plane), which was not surprising as the incorporation of small Na$^+$ cations (ionic radius of 116 pm) at the A-site could lead to unit cell contraction.$^{27}$ This lattice contraction was further confirmed by X-ray photoelectron spectroscopy (XPS) measurements, which showed increased Pb-Br interaction as a result of reduced bond length. As shown in figures 2e and 2f, the Br 3d$_{5/2}$ and 3d$_{3/2}$ as well as Pb 4f$_{7/2}$ and 4f$_{5/2}$ orbitals of CsPbBr$_3$–Na shifted to higher binding energies by 0.2 eV in
reference to CsPbBr$_3$. In contrast, the diffraction peaks for the samples EDA5 and EDA5-Na displayed small shifts to lower angles, as a result of unit cell expansion. Figures 2 c, d show pseudo Voight fitting curves for the diffraction peaks of the (121) and (202) crystallographic planes, respectively. This shift of diffraction peaks could be well explained to result from the incorporation of large EDA$^{2+}$ cations (ionic radius 333 pm) within the 3D perovskite structure, which has previously been shown in other halide perovskites.$^{28, 29, 30, 31, 32}$ Two mechanisms were proposed to explain the lattice expansion and increase of band gap upon the incorporation of large organic cations. One attributed it to the lattice strain caused by Pb-I bond elongation (in EDA$^{2+}$ alloyed methylammonium lead iodide), and the other to a hollow 3D structure, in which incorporation of EDA$^{2+}$ cations lead to the formation of randomly oriented Pb$^{2+}$ vacancies.$^{28}$ As the valence band maximum of ABX$_3$ type 3D halide perovskites is an antibonding hybrid state of the metal s and halide p orbitals, reduced interaction of the B$^{2+}$ and X$^-$ ions, due to either bond elongation or discontinuities, would lead to the increasing of the energy band gap.$^{33}$

**Figure 3 | Structural characterization of thin films.** a, Selected area electron diffraction patterns of thin films. b, XRD patterns of thin films. c, Pseudo Voight peak fitting of the diffraction peaks for the (121) crystallographic plane of thin films. d, Pseudo Voight peak fitting of the diffraction peaks for the (202) crystallographic plane of thin films. e, Br 3d peak and
gaussian fitting of 3d_{5/2} and 3d_{3/2} peaks. Pb 4f peak and Voight fitting of 4f_{5/2} and 4f_{7/2} peaks.

XPS spectra were employed to probe changes of the Pb-Br interactions in the samples EDA5 and EDA5-Na. The Pb-Br bond elongation led cell expansion would cause shifts of the Pb 4f and Br 3d electron orbitals to lower binding energies\(^{34,35}\), without the change of the Br/Pb ratio. While the creation of Pb\(^{2+}\) vacancies would cause an increase in the Br/Pb ratio, without the change of the binding energies of the core levels of both ions. The XPS results for EDA5 show that the binding energies of Pb 4f_{5/2} and 4f_{7/2}, as well as Br 3d_{3/2} and Br 3d_{5/2}, are almost the same as those of CsPbBr\(_3\) (figure 3e, f). While quantitative analysis of the XPS spectra showed Br/Pb ratio increased significantly with the incorporation of EDA\(^{2+}\) (~3.97 for the sample EDA5) as compared to the sample CsPbBr\(_3\) (~2.27), suggesting the formation of Pb\(^{2+}\) vacancies and hollow 3D structure. We attribute the below-nominal Br/Pb ratio in pure CsPbBr\(_3\) to the presence of high surface defect density as corroborated by the short average PL decay lifetime. Energy dispersive x-ray fluorescence was also conducted to probe the relative concentrations of Pb\(^{2+}\) and Br\(^-\) in the studied samples. As can be seen from Supplementary figure 5, the intensity of Br K\(_{\alpha1}\) and Br K\(_{\beta1}\) lines for EDA5 and EDA5-Na were substantially higher than those for CsPbBr\(_3\) and CsPbBr\(_3\)-Na. Moreover, EDA5 also displayed slightly stronger Pb L\(_{\alpha1}\) and Pb L\(_{\beta1}\) peaks compared to CsPbBr\(_3\), CsPbBr\(_3\)-Na and EDA5-Na. To quantify the molar ratios between the different components, the intensity vs concentration scatter plots for the standards (fit using a linear equation) were used as calibration curves (Supplementary figure 6). The raw intensity (cps), the calculated concentrations (ppm and M) and the molar ratios of the different components in the studied samples are given in
Supplementary table 4. From these results, we observe a similar trend to what was observed from the XPS analysis. That is, Br/Pb ratio significantly increased from the nominal 3:1 ratio with the introduction of EDA\(^{2+}\) and EDA\(^{2+}\) along with NaBr. This confirms the formation of Pb\(^{2+}\) vacancies.

The blue-shift of emissions for the CsPbBr\(_3\) thin films upon the addition of EDABr\(_2\) is consistent with what was observed in hollow 3D MASnI\(_3\), MAPbI\(_3\) and FASnI\(_3\) perovskites.\(^{28, 29, 30}\) Increasing the EDA\(^{2+}\) content also led to decreasing crystal grain sizes, as evidenced by the XRD peak broadening in Supplementary figure 7. The nanocrystal formation and surface defect passivation by EDA\(^{2+}\) cations resulted in significantly increased PLQEs, with the highest value recorded for the hollow 3D CsPbBr\(_3\) at ~ 81\%.

Overall, EDA\(^{2+}\) cations are capable of forming small crystalline domains of CsPbBr\(_3\), passivating their surfaces, and penetrating into the lattice to form hollow 3D structures. Further lattice expansion was observed for the sample EDA5-Na, which showed significantly blue shifted emission as compared to the other samples. We suppose Na\(^+\) cations occupy interstitial sites within the perovskite structure as has been reported for alkali ions in organo-metal halide perovskites,\(^{36}\) because Na\(^+\) cations are too small to create more Pb\(^{2+}\) vacancies as seen with EDA\(^{2+}\). A slight shift to higher binding energies was also observed for Br 3d\(_{5/2}\) and 3d\(_{3/2}\) as well as Pb 4f\(_{7/2}\) and 4f\(_{5/2}\) core orbitals of EDA5-Na. Because of the increased lattice parameter for EDA5-Na, improved orbital overlap between Pb\(^{2+}\) and Br\(^-\) ions cannot explain the observed peak shift in the photoelectron spectra. However, the presence of interstitial defects has been shown to result in increased lattice parameters and XPS peak shift to higher binding energies in other
systems, such as silicon.\textsuperscript{37} Thus, we ascribe the XRD shift to lower diffraction angle and XPS shift to higher binding energy to the presence of Na\textsuperscript{+} interstitials.

In order to directly visualize the effects of the different ions on the microstructural properties of these samples, we used transmission electron microscopy (TEM) and high resolution TEM (HRTEM) to characterize the microstructures. As shown in Figures 4a, TEM images of CsPbBr\textsubscript{3}-Na, EDA5 and EDA5-Na clearly indicate the formation of perovskite NCs. Particle size distribution analysis revealed median sizes of around 40 nm, 12 nm, and 17 nm for CsPbBr\textsubscript{3}-Na, EDA5 and EDA5-Na, respectively. As the median particle size of EDA5-Na is still much larger than the exciton bohr radius of CsPbBr\textsubscript{3} (\textasciitilde 7 nm), blue emission from small quantum confined CsPbBr\textsubscript{3} NCs could not be the case here. With HRTEM, large pores at the center of CsPbBr\textsubscript{3} NCs with a median size of 4.25 nm were observed in EDA5-Na. These CsPbBr\textsubscript{3} NCs with pores, or hollow NCs, could be clearly observed throughout the whole film (Supplementary figures 8a-d). These hollow NCs were not present in CsPbBr\textsubscript{3}-Na or EDA5, as can be gathered from the TEM images shown in Supplementary figure 9 and the HRTEM images in figure 3b. The median shell thickness of these hollow CsPbBr\textsubscript{3} NCs was found to be 6.5 nm as illustrated in Supplementary figure 8c. This shell thickness is slightly larger than the grain size needed for CsPbBr\textsubscript{3} to possess an emission energy of \textasciitilde 2.6 eV (\textasciitilde 477 nm), i.e. \textasciitilde 6 nm.\textsuperscript{5} However, recalling that the shell of these hollow nanocrystals have a hollow 3D perovskite crystal structure, as per the XRD results, we ascribe the observed optical band gap widening and emission peak shift to the quantum confined hollow perovskite shell. These hollow nanostructures perfectly explain how the optical band gap of CsPbBr\textsubscript{3} NCs could be tuned as a result of quantum size effect and a hollow perovskite crystal
structure, while the size of the NC grains was still well above the exciton bohr radius of ~7 nm.

The TEM and HRTEM images were further analyzed to confirm that the “lighter” regions were not results of inter-grain voids, sample preparation artifacts or electron beam damage. As shown in Supplementary figure 10, fast Fourier transform of TEM and STEM images of mono-grain hollow nanocrystals show single sets of spots indicating the single crystalline nature of these nanocrystals. Moreover, the absence of spots from multiple grains conclusively proves that the pores are not a result of inter-grain voids. To exclude the TEM sample preparation as the source of the observed unique microstructures, we conducted the TEM characterization using an alternative technique depicted in Supplementary figure 11. The collected TEM images are consistent with what was observed using the scratch and sonicate TEM sample preparation technique, confirming that these microstructures are not sample preparation artifacts. Moreover, the low contrast regions in these grains do not resemble the products reported to arise from electron beam damage (Pb rich nanoparticles).\(^{38}\) In addition, as shown in Supplementary figure 12, TEM images taken 10 s apart for a total of 60 s show that there is little change in the microstructure of the sample, indicating that the pores are not results of electron beam damage.
Figure 3 | TEM characterization. a, TEM images of CsPbBr$_3$-Na, EDA5 and EDA5-Na thin films. Inset: particle and pore size distribution of NCs. b, HRTEM images of CsPbBr$_3$-Na, EDA5, and EDA5-Na thin films. Inset: Simulated HRTEM images showing lattice fringes for the (101) planes.

Discussion

Previous studies on hollow NCs have attributed their formation to nanoscale Kirkendall effect$^{21,39}$, Ostwald ripening$^{24}$, galvanic replacement$^{23}$ and cation exchange$^{22}$. To gain a better understanding on what could be diffusing in and out of the core of CsPbBr$_3$ NCs, we used a combination of XPS and energy-dispersive X-ray spectroscopy (EDX) to probe the positions of ions. It was found that electrons from Cs 3d$_{5/2}$, C 1s of C-N bond and N 1s orbitals were detectable in XPS (Supplementary figure 13 and figure 14a), indicating the presence of Cs$^+$ and EDA$^{2+}$ ions on or near the surface. While electrons from Na 1s orbital were readily discernable in XPS for CsPbBr$_3$-Na, Na 1s peak in EDA5-Na was not
observed (Supplementary figure 14b). In contrast, EDX spectrum of EDA5-Na confirmed
the presence of Na\(^+\) ions within the sample (Supplementary figure 15). These results
suggest that Na\(^+\) cations were located deep in the shell or within the core of the hollow
NCs. Based on the changes observed in the unit cell volume, surface chemistry and
microstructure of the hollow NCs as compared to the regular NCs, we propose a
mechanism as shown in Figure 4a, in which the diffusion of Na\(^+\) ions from the surface to
the core selectively draws Br\(^-\) anions from the perovskite lattice to the surface,\(^{40}\) reducing
the coordination number of Pb\(^{2+}\) cations. This is supported by the increased Br/Pb ratio
observed in EDA5-Na compared to that of EDA5. Because undercoordinated ions
generally display higher free energy compared to those that are fully coordinated, Pb\(^{2+}\)
ions will likely diffuse to lattice sites with higher coordination number driven by the free
energy landscape. Although the diffusion of Pb\(^{2+}\) ions has been reported to possess a high
diffusion barrier of \(\sim 2.3\) eV, the presence of Pb\(^{2+}\) vacancies due to the incorporation
EDA\(^{2+}\) could lower this energy barrier.\(^{41}\) The diffusion of Pb\(^{2+}\) cations will be associated
with vacancy migration in the opposite direction resulting in vacancy coalescence and
void formation. To further validate the proposed mechanism, we introduced NaBr before
thin film deposition in the form of a 20 nm thin film on glass substrate. The EDA5
precursor was then deposited on top of the NaBr layer. The obtained thin film displayed a
broad PL spectrum that can be deconvoluted to the spectra of EDA5 and EDA5 – 2\% as
shown in Supplementary figure 16c. This result indicates that, Na\(^+\) ions can diffuse into
the EDA5 thin film to form hollow nanocrystals. Overall, the effects of individual
additives (NaBr and EDABr\(_2\)) and their combination on the morphological and optical
properties of CsPbBr\(_3\) can be summarized in figure 4b: the addition of only Na\(^+\) has little-
to-no effect on the crystalline lattice, the addition of only $\text{EDA}^{2+}$ creates hollow 3D structures and the addition of both $\text{Na}^+$ and $\text{EDA}^{2+}$ leads to the formation of hollow perovskite NCs.

**Figure 4 | Proposed formation mechanism and crystal structures.** a, proposed formation mechanism of hollow $\text{CsPbBr}_3$ NCs beginning from $\text{Na}^+$ and $\text{Br}^-$ diffusion from the surface to the core and vice versa, respectively, followed by $\text{Pb}^{2+}$ diffusion via $\text{Pb}^{2+}$ vacancies culminating in vacancy condensation b, changes of the crystal structures of $\text{CsPbBr}_3$ upon the additions of $\text{NaBr}$, $\text{EDABr}_2$ and both $\text{NaBr}$ and $\text{EDABr}_2$. 

With the understanding of the roles of the different ions, we demonstrated rational control of the particle and pore sizes of CsPbBr$_3$ hollow NCs, and subsequently their optical properties, by controlling the Na$^+$ and EDA$^{2+}$ contents. As shown in Supplementary figures 17a-i, the increase in Na$^+$ content (in the presence of EDA$^{2+}$ 1:1 with the perovskite precursors) had no significant effect on grain size, but generally led to larger pore sizes from a median pore size of 3.2 nm for samples with 1 mol % NaBr to 4.8 nm for those containing 4 mol % of NaBr. This pore size increase in turn resulted in a narrower shell thickness and a corresponding optical band gap widening. Conversely, increasing the EDA$^{2+}$ concentration (in the presence of Na$^+$) had no obvious influence on the pore size, but led to the reduction of the particle sizes. As shown in Supplementary figures 18a-f, the median particle size decreased from 19 nm to 17 nm for the samples prepared with of 0.4 and 1.2 molar ratios of EDABr$_2$, while keeping the NaBr content constant at 3 mol %.

In summary, by carefully choosing appropriate organic and alkali metal salts, light emitting thin films containing hollow perovskite nanocrystals can be prepared via facile solution processing. The organic cations not only penetrate into the perovskite lattice to create vacancies, but also passivate the surfaces of the perovskite nanocrystals. The small alkali metal cations can diffuse throughout the perovskite lattice to assist the formation of hollow structures with the presence of large organic cations. As a result, quantum confinement can be realized in hollow perovskite nanocrystals with controlled pore sizes and shell thicknesses, which exhibit highly tunable emissions with high photoluminescence quantum efficiencies. Our work represents a groundbreaking advance
in the field of metal halide perovskite nanocrystals, from well-developed nanostructures with positive curvatures to novel hollow structures, which will stimulate exploration of other nanostructures with remarkable and unique properties. Applications of hollow perovskite nanocrystals in various types of optoelectronic devices are envisioned in the near future.

**Methods**

**Materials.** Lead (II) bromide (99.999 %), cesium bromide (99%), ethylenediamine (99 %), hydrobromic acid (48 wt. % in H₂O), sodium bromide (99 %) and dimethyl sulfoxide (99.9%) were purchased from Sigma-Aldrich. All reagents and solvents were used without further purification unless otherwise stated.

**Synthesis of C₂N₂H₁₀Br₂ (EDABr₂).** Ethylenediamine (1 equiv.) and 48 wt. % hydrobromic acid (2.1 equiv.) were combined in ethanol at 0 °c. After 30 minutes, white precipitate was extracted through evaporation of the solvent using a rotary evaporator. The white precipitate was washed with diethyl ether twice and was left to dry in a desiccator overnight before use. The salt was stored in a glovebox.

**Thin film processing.** 0.2 mmol CsBr and 0.2 mmol PbBr₂ were dissolved in 1 ml of DMSO to make the perovskite precursor solution. EDABr₂ was added to the perovskite precursor solution in varying concentrations from 0 to 1.2 molar ratio. The Na⁺ content in the perovskite precursor solution was controlled by varying the amount of NaBr from 0 to 4 mol%. ITO substrates were purchased from Thin Film Devices. Before use, they were
sequentially cleaned by sonication in detergent (Hellmanex III) water, deionized water, acetone and isopropanol for 15 minutes and were dried in an oven overnight. The substrates were then cleaned under UV-Ozone treatment and transported into a glovebox for one-step spin coating of the precursor solution at 3000 RPM for 60 s. Subsequently, the films were annealed at 100 °C for 20 minutes.

**Atomic Force Microscopy.** AFM images were taken on a Bruker Icon scanning probe microscope in tapping mode.

**Photoluminescence spectroscopy.** Steady-state PL was carried out using an Edinburgh FS5 steady state spectrometer with a 150 W xenon lamp at an excitation wavelength of 365 nm. TRPL was collected using Time Correlated Single Photon Counting (TCSPC) for 10,000 counts. Excitation was provided by an Edinburgh EPL-360 picosecond pulsed diode laser. The PL decay was fit using a triple-exponential decay function. The average lifetime was obtained from the tri-exponential decays according to equation 1.

$$\tau_{ave} = \frac{\Sigma a_i \tau_i^2}{\Sigma a_i \tau_i}, \quad i = 1, 2, 3$$  \(1\)

where $\tau_i$ represents the decay time and $a_i$ represents the amplitude of each component.

**Absorption spectrum measurements.** Absorption spectra were obtained using an Agilent Technologies Cary 5000 UV-Vis-NIR spectrophotometer.

**Photoluminescence quantum efficiency (PLQE).** PLQE measurements were performed in accordance to what has been reported previously.\textsuperscript{42} Briefly, a Hamamatsu Quantaurus-QY Spectrometer (Model C11347-11) equipped with a xenon lamp, an integrating sphere sample chamber and a CCD detector. The PLQEs were calculated by the equation: $\eta QE = \frac{\Sigma a_i \tau_i}{\Sigma a_i \tau_i}$.
\[ \frac{I_s}{E_R-E_s} \], in which \( I_s \) represents the luminescence emission spectrum of the sample, \( E_R \) is the spectrum of the excitation light for the reference (empty substrate), and \( E_s \) is the excitation spectrum for exciting the sample. The PLQE measurements were done consecutively and a density of 0.3 mW/cm\(^2\) at an excitation wavelength of 365 nm was used for all samples.

**Powder X-ray diffraction (XRD).** XRD patterns were obtained using a Siemens D500 powder diffractometer equipped with a Cu K\(\alpha\) x-ray source. Diffraction patterns were recorded from 5° to 40° 2\(\theta\) with a step size of 0.05° under a tube current of 30 mA and tube voltage of 40 KV.

**Transmission Electron Microscopy images (TEM).** Microstructural characterization was performed using transmission electron microscopy (TEM), on a JEOL JEM-ARM200cF at 200kV. TEM samples were prepared by scraping thin films from substrate and dispersing the powder in a non-polar solvent (Hexane). The dispersion was sonicated for 10 minutes to ensure uniform distribution before dropping it on a 200 mesh Cu grid. Alternatively, Cu grids were pressed face-down on thin films prepared on PDMS substrates, followed by applying a single drop of 2-propanol on the Cu grid. The Cu grids were then picked up using fine tweezes before the solvent completely evaporated. TEM image analysis was performed in Gatan microscopy software suite.

**X-ray photoelectron spectroscopy (XPS).** XPS was conducted using a PHI 5000 series XPS equipped with a dual anode x-ray source. For our purpose, Al K\(\alpha\) radiation with a photon energy of 1486.6 eV at a take-off angle of 45° and a pass energy of 35.75 eV were used. Charge compensation was performed using adventitious C 1s peak (284.6 eV).
Spectra background were fit and subtracted using an integrated Shirley function. XPS curves were deconvoluted using a Voight peak function for metal core electron spectra and gaussian peak functions for the rest.

**Energy Dispersive X-ray Fluorescence.** EDXRF was performed using a Panalytical Epsilon 3 spectrometer equipped with a rhodium X-ray tube and a silicon drift detector.

**Data Availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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**Author Contributions** M.W., Y.T. and B.M. conceived the experiments. M.W. and B.M. analyzed and interpreted the data. M.W., C.Z. and H.L. synthesized organic salts; M.W. prepared thin film samples and collected XRD, XPS and AFM data; M.W., M.C., D.B. and Y.Z. measured the photophysical properties; M.W. and L.X. prepared TEM samples; Y.X. performed TEM experiment; M.W. and Q.H. performed image analysis on TEM data. X.L. and MW performed and analyzed EDXRF. The manuscript was written by M.W. and B.M. The project was planned, directed and supervised by B.M. All authors discussed the results and commented on the manuscript.

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Supplementary Information

Hollow Metal Halide Perovskite Nanocrystals with Efficient Blue Emissions

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Supplementary Figure 1| Atomic Force Microscopy images of CsPbBr3 thin films containing 3 mol % of NaBr and a. 0.2, b. 0.4, c. 0.6, d. 0.8, e. 1.0 and f. 1.2 molar ratio of EDABr2.

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Supplementary Figure 2 | Thin film thickness

a. An AFM image of a scratched section of a thin film, b. height profile of a transverse section of the corresponding AFM images for CsPbBr$_3$ thin films containing 3 mol % NaBr and varying concentrations of EDABr$_2$.

Supplementary Figure 3 | Photophysical properties of CsPbBr$_3$ thin films with 1:1 ratio of EDABr$_2$:CsPbBr$_3$ with varying contents of NaBr.

a. Photoluminescence spectra b, PLQE and emission peak wavelength
Supplementary Figure 4 | Photoluminescence spectra of CsPbBr$_3$ thin films. a, containing only NaBr and not EDABr$_2$ b, containing EDABr$_2$ and not NaBr.

Supplementary Table 1 | Composition and photophysical properties of samples with varying EDABr$_2$ content

| Sample | Composition (CsPbBr$_3$: EDABr$_2$: NaBr) | $\lambda_{em}$ (nm) | FWHM (nm) | $\Phi$ (%) | $\tau_{avg}$ (ns) |
|--------|-------------------------------------------|---------------------|------------|------------|------------------|
| EDA2-Na | 1 : 0.4 : 0.03 | 498 | 26 | 2.1 | 21 |
| EDA4-Na | 1 : 0.8 : 0.03 | 480 | 25 | 52.2 | 123 |
| EDA6-Na | 1 : 1.2 : 0.03 | 471 | 25 | 48.7 | 146 |

Supplementary Table 2 | Composition and photophysical properties of samples with varying NaBr content
| Sample   | Composition  | \(\lambda_{em}\) (nm) | FWHM (nm) | \(\Phi\) (%) | \(\tau_{avg}\) (ns) |
|----------|--------------|------------------------|-----------|--------------|---------------------|
| 1% NaBr  | 1 : 1 : 0.01 | 488                    | 22        | 72.1         | 119                 |
| 2% NaBr  | 1 : 1 : 0.02 | 483                    | 24        | 73.8         | 115                 |
| 4% NaBr  | 1 : 1 : 0.04 | 459                    | 30        | 32           | 140                 |

Supplementary Table 3 | Atomic concentrations of samples through XPS

| Sample      | Composition  | Br/Pb ratio |
|-------------|--------------|-------------|
| (CsPbBr\(_3\): EDABr\(_2\): NaBr) |
| CsPbBr\(_3\)       | 1 : 0 : 0     | 2.274       |
| CsPbBr\(_3\) – Na  | 1 : 0 : 0.03  | 2.329       |
| EDA5         | 1 : 1 : 0     | 3.965       |
| EDA5 - Na    | 1 : 1 : 0.03  | 4.408       |
Supplementary Figure 5 | Energy Dispersive X-ray fluorescence.

Supplementary Figure 6 | Calibration curves for EDXRF of a, Cs⁺. b, Pb²⁺. c, Br⁻.
## Supplementary Table 4 | Quantitative analysis results of EDXRF.

| Sample      | Ion   | Intensity (cps) | Concentration (ppm) | Molarity(M) | Molar ratio |
|-------------|-------|----------------|---------------------|-------------|-------------|
| CsPbBr₃     | Cs⁺   | 18.9461        | 19.032              | 0.1432      | 0.81        |
|             | Pb²⁺  | 126.189        | 36.6241             | 0.17676     | 1           |
|             | Br⁻   | 350.7068       | 44.652              | 0.55882     | 3.16        |
| CsPbBr₃ – Na | Cs⁺   | 21.70129       | 31.54               | 0.23731     | 1.37        |
|             | Pb²⁺  | 122.9492       | 35.7644             | 0.17261     | 1           |
|             | Br⁻   | 339.0205       | 42.935              | 0.53733     | 3.11        |
| EDA5        | Cs⁺   | 23.52054       | 39.8                | 0.29946     | 1.30        |
|             | Pb²⁺  | 167.4043       | 47.56               | 0.22954     | 1           |
|             | Br⁻   | 706.289        | 96.8828             | 1.21249     | 5.28        |
| EDA5 – Na   | Cs⁺   | 23.07229       | 37.766              | 0.28416     | 1.85        |
|             | Pb²⁺  | 108.2174       | 31.855              | 0.15374     | 1           |
|             | Br⁻   | 519.2921       | 69.4152             | 0.86873     | 5.65        |
Supplementary Figure 7 | XRD characterization of thin films with varying EDABr$_2$ content
Supplementary Figure 8 | Microstructural characterization of EDA5-Na. a, b TEM images of EDA5-Na c, HRTEM image of EDA5-Na (inset: shell thickness size distribution). d, HAADF-STEM image of EDA5-Na.
**Supplementary Figure 9** | TEM images of a, CsPbBr$_3$-Na b, EDA5.

**Supplementary Figure 10** | Mono-grain hollow nanocrystals. A, TEM image of a mono-grain hollow NC (inset: FFT of the marked region). b, STEM image of a mono-grain hollow NC (inset: FFT of marked region).
Supplementary Figure 11 | Alternative TEM sample preparation. a, Cu grid was pressed on thin films formed on PDMS substrate followed by 2-propanol dropping then the Cu grid was picked up with fine tweezers before solvent evaporation. b, representative sample under TEM using the described technique. TEM images at c, 100K, d. 200 K and d. 500K magnification

Supplementary Figure 12 | TEM image as a function of electron beam irradiation time
Supplementary Figure 13 | XPS characterization of thin films. a, Cs 3d peak and Voight fitting of 3d_{5/2} and 3d_{3/2} peaks b, C 1s peak and gaussian fitting of C-C C 1s and C-N C 1s peaks.

Supplementary Figure 14 | XPS characterization of thin films. a, N 1s peak and gaussian fitting of N 1s peak b, Na 1s peak and gaussian fitting Na 1s peak.
Supplementary Figure 15 | Energy-dispersive x-ray spectroscopy of EDA5-Na.

Supplementary Figure 16 | Alternative processing of hollow nanocrystal thin films. 

a, scheme showing EDA5 thin film cast on 20 nm NaBr layer which under annealing activates Na⁺ diffusion from the NaBr layer to the EDA5 layer to form and EDA5-Na thin film. 
b, UV-Vis absorption spectrum of the processed thin film. 
c, PL spectrum of as-formed film fit and deconvoluted to the sum of EDA5 and EDA5-2% spectra.
Supplementary Figure 17 | The effect of NaBr content on microstructure. TEM images of CsPbBr$_3$ containing EDABr$_2$ in a 1:1 ratio and a, 1 mol% NaBr b, 2 mol% NaBr c, 4 mol% of NaBr. HRTEM images of d, 1 mol% NaBr e, 2 mol% NaBr f, 4 mol% of NaBr. Particle and pore size distributions of g, 1 mol% NaBr h, 2 mol% NaBr i, 4 mol% of NaBr.
**Supplementary Figure 18 | The effect of EDABr$_2$ content on microstructure.** TEM images of CsPbBr$_3$ containing 3 mol% of NaBr and EDABr$_2$:CsPbBr$_3$ ratio of a, 0.4 b, 1.2. HRTEM images of EDABr$_2$:CsPbBr$_3$ ratio of c, 0.4 d, 1.2. Particle and pore size distributions of CsPbBr$_3$ containing 3 mol% of NaBr and EDABr$_2$:CsPbBr$_3$ ratio of e, 0.4 f, 1.2.
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