

### Article

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# Solvothermal Synthesis of Ultrathin Cesium Lead Halide Perovskite Nanoplatelets with Tunable Lateral Sizes and Their Reversible Transformation into Cs<sub>4</sub>PbBr<sub>6</sub> Nanocrystals

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**ABSTRACT:** The versatility of perovskite crystal structure has become the great advantage of lead halide perovskite nanocrystals (NCs) during their functional applications. Here we report an effective solvothermal method for the controllable synthesis of CsPbBr<sub>3</sub> nanoplatelets (NPLs) and their transformation to Cs<sub>4</sub>PbBr<sub>6</sub> NCs. Through solvothermal reaction of a mixture of Cs-oleate and PbBr<sub>2</sub> precursors, CsPbBr<sub>3</sub> NPLs can be synthesized in mass production. The lateral sizes of CsPbBr<sub>3</sub> NPLs can be precisely tuned by varying the solvothermal reaction temperatures and times, while the thickness of NPLs keeps constantly at ~4.2 nm, which is in quantum confinement regime. The fine-tuning of lateral NPLs sizes results in precise modulation of their photoluminescence emission. Moreover, an interesting phase transformation from cubic CsPbBr<sub>3</sub> NPLs to rhombohedral Cs<sub>4</sub>PbBr<sub>6</sub> NCs, and the reversible transformation from Cs<sub>4</sub>PbBr<sub>6</sub> NCs to CsPbBr<sub>3</sub> NPLs can be readily achieved by changing the solvothermal reaction sources. The present solvothermal approach is simple, convenient, controllable, and can be easily extended to preparation of other perovskite NCs with different halide compositions.

#### INTRODUCTION

Lead halide perovskite nanocrystals (NCs) recently have gained huge interest due to their outstanding optical and electronic properties, thus have shown great potential for applications in light-emitting diodes (LEDs),<sup>1-5</sup> photovoltaic cells,<sup>6, 7</sup> photodetectors,<sup>8-10</sup> etc. Due to the intrinsic instability and soft nature, lead halide perovskite NCs can be synthesized in a variety of sizes, shapes, and compositions,<sup>11-13</sup> such as organic-inorganic hybrid perovskites CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub> (X=Cl, Br, I)<sup>15-17</sup> and all-inorganic perovskites CSPbX<sub>3</sub> (X=Cl, Br, I)<sup>18, 19</sup> in various morphologies (quantum dots,<sup>18</sup> nanowires,<sup>12, 21</sup> nanoplatelets,<sup>22, 23</sup> nanocubes,<sup>24, <sup>25</sup> etc). The versatility of perovskite crystal structure has become the great advantage of lead halide perovskite NCs for their functional applications.</sup>

Precisely control over the morphology, structure and composition of lead halide perovskite NCs not only offers great opportunity for accessing novel nanostructures, but also allows for understanding the growth evolution of NCs and establishing their structure-property link. Since the pioneering work reported by Kovalenko group,<sup>18, 26, 27</sup> the research on controllable synthesis of all-inorganic CsPbX<sub>3</sub> NCs with tailored morphology and structure has ACS Paragon attracted increased attention. In 2015, Kovalenko group reported the synthesis of CsPbX, NCs by an air-free hot injection method. The halide compositions can be easily changed via ion-exchange transformations, resulting in the tunable photoluminescnece (PL) emission.<sup>18</sup> Deng group developed a ligand-mediate reprecipitation method for manipulating the shape of CsPbX<sub>3</sub> NCs. Diverse CsPbX<sub>3</sub> NCs, including quantum dots, nanocubes, nanorods and nanoplatelets (NPLs), have been synthesized and shown distinct shape-dependent PL emissions.<sup>20</sup> Moreover, Manna group reported the interesting monolayer-level thickness control over CsPbBr<sub>3</sub> NPLs to achieve thickness-dependent PL emission.<sup>28</sup> Very recently, the chemical transformation of CsPbBr<sub>3</sub> NCs to get a new kind of lead-halide depleted perovskite derivative, i.e. Cs<sub>4</sub>PbX<sub>6</sub> NCs, has also attract much attention.<sup>29-31</sup> The Cs<sub>4</sub>PbX<sub>6</sub> phase has been considered as a type of zerodimensional perovskite, showing a differently insulator bandgap.<sup>32, 33</sup>

Although great efforts have been devoted to the controllable synthesis of lead halide perovskite NCs, many challenges still remain. The air-free hot injection method has been considered as the most mature approach for Environment

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synthesis of CsPbX, NCs.<sup>11, 18, 27, 34</sup> However, the rapid reaction in very short time is not facilitate for the controllable synthesis. With the aim of precisely control over such tiny NCs, a relatively mild crystal growth environment is favorable. <sup>35</sup> In this paper, we develop a facile solvothermal method for the controllable synthesis of CsPbBr<sub>3</sub> NPLs and their transformation to Cs<sub>4</sub>PbBr<sub>6</sub> NCs. The readily effective method results in the production of uniform CsPbBr, NPLs in a large-scale. Owing to the sealed environment of the solvothermal method, there is no extra procedures for an inert atmosphere which are usually necessary in the other methods.<sup>18, 20</sup> In the solvothermal synthesis, the reaction between Cs-oleate and PbBr<sub>2</sub> precursors can take place at relatively low temperatures and the kinetics of the reaction can also be depressed. As a result, we can succeed in achieving monodisperse CsPbBr, NPLs with precisely tuned lateral sizes by simply adjusting the reaction times or temperatures. In addition, we demonstrate that the developed solvothermal method can be extended for further structure and composition control over the cesium lead halide NCs. An successful reversible transformation between CsPbBr<sub>3</sub> NPLs and Cs<sub>4</sub>PbBr<sub>6</sub> NCs can be achieved by simply changing the amount of Csoleate or PbBr, precursors.

#### **RESULTS AND DISCUSSION**

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The CsPbBr<sub>3</sub> NPLs were prepared by a solvothermal method using a mixture of Cs-oleate and PbBr<sub>2</sub> precursors at relatively low temperatures (6o-180 °C). Detailed synthetic conditions are shown in Supporting Information. The proposed growth process has been illustrated in **Scheme 1.** Firstly, PbBr<sub>2</sub> was dissolved into the octadecene (ODE)/oleylamine (OLA)/oleic acid (OA) solution to get a PbBr<sub>2</sub> precursor. After dissolving of Cs<sub>2</sub>CO<sub>3</sub> into ODE/OA, Cs-oleate precursor was also generated. The precursors were fully mixed together at room temperature and then transferred into an autoclave. After solvothermal reaction, CsPbBr<sub>3</sub> NPLs were obtained. All the operations were completed in ambient atmosphere.

The perovskite phase of as-prepared sample has been confirmed by powder X-ray diffraction (XRD) analysis. As shown in Figure 1a, the diffraction pattern can be well indexed into cubic CsPbBr, (PDF card No. 54-752). No other phases were detected, suggesting the high purity of the product. Transmission electron microscopy (TEM) image shown in Figure 1b indicates that the CsPbBr, product has regular NPL morphology. The sharp edges suggest a single crystalline nature for each NPL. The small black spots existing in the NPLs are metallic lead nanoparticles, which can be confirmed by the HAADF-STEM image (Figure S1). Similar lead nanoparticles have also been observed in other previously reported CsPbBr<sub>3</sub>NCs, <sup>28</sup> MAPbBr, sheets<sup>36</sup> and CsPbBr, nanosheets<sup>37</sup>. Through characterization of high-resolution TEM (HRTEM) image of perpendicularly oriented NPLs (Figure 1c), the thickness of NPLs can be estimated to be ~4.2 nm, corresponding to 7 monolayers of CsPbBr<sub>3</sub>.<sup>38</sup> Figure 1d shows a photo image of as-prepared product dispersed in n-hexane. The

solution displays yellow color with a very high concentration (right), suggesting large-scale production of CsPbBr<sub>3</sub> NPLs. The diluted NPLs dispersion (50 times diluted) shows a brighter yellowish green color (left). A ~0.192 g amount of yellow powder was successfully fabricated per single experimental run (**Figure** 1e), implying that the CsPbBr<sub>3</sub> NPLs synthesized by the solvothermal method are easy to achieve mass production.

After continuously dilution from the diluted CsPbBr, dispersion (shown in left of Figure 1d) for about 50 times, the obtained solution was used for testing of their spectral properties. Figure 1f shows the UV-vis absorption, PL emission and excitation spectra of the CsPbBr<sub>3</sub> NPLs. The characteristic absorption peak is located at ~449 nm. The excitation spectrum exhibits an excitation peak at ~448 nm, which is in good agreement with the UV-vis absorption result. The emission spectrum consists of a narrow emission peak centered at ~456 nm. Because of the size of CsPbBr<sub>3</sub> NPLs relative to its exciton Bohr diameters (~7.0 nm), the observed blue shift of CsPbBr, relative could be explained by the quantum confinement effect.<sup>38</sup> PL quantum yield (QY) measurements show a high QY of ~50% for the as-prepared CsPbBr<sub>3</sub> NPLs, which is higher than bulk crystal 40 and CsPbBr, nanosheets.28, 41 The high PLQY could be related to a low density of trap states in the present NPLs.<sup>39</sup> The PL decay curve of the NPLs is shown in Figure 1g, which can be fitted well with the triexponential decay function. The estimated average PL lifetime is of ~4.87 ns, which is comparable with those of previously reported CsPbBr<sub>3</sub> NPLs (~3-4.3 ns).<sup>28, 39</sup>

Interestingly, the optical properties of the CsPbBr, NPLs can be precisely controlled by simply changing the solvothermal reaction times, as displayed in Figure 2a. With an increase of reaction time, the emission peak shifts from 453 nm to 465 nm, implying that our approach can achieve more precise modulation of PL emissions of perovskite CsPbBr<sub>3</sub> as compared with other reported synthetic methods.<sup>24, 27, 42</sup> <sup>43</sup> Figure 2b show the UV-vis absorption and PL emission spectra of CsPbBr<sub>3</sub> NPLs prepared at different reaction times. CsPbBr<sub>3</sub> NPLs with tunable absorption peak positions ranging from 446 nm to 460 nm could be achieved by varying the reaction time from 30 min to 24 h. We also measured the PL lifetimes of the different CsPbBr<sub>2</sub> samples (Figure S<sub>2</sub>). As the reaction time increases, the lifetime of NPLs increases slightly from 3.2 ns to 9.9 ns. There is no significant change in the PLQY from 39% to 52% (Figure S<sub>3</sub>), indicating that prolonged solvothermal reaction time did not cause excessive surface defects in the CsPbBr<sub>3</sub> NPLs.

TEM images of the CsPbBr<sub>3</sub> samples are shown in **Figure 2**c-f. All of the products consist of numerous regular NPLs with good monodispersity and uniform size. With an increase of reaction time, the shape of the NPLs gradually changes from narrow rectangle into square. The average later dimensions change from 100.7  $\pm$  9.4 nm \* 15.2  $\pm$  5.3 nm to 44.1  $\pm$  3.8 nm \* 42.4  $\pm$  5.9 nm (**Figure 2**g-j), indicating that the lateral size control can be well achieved



Scheme 1. Schematic diagram of solvothermal synthesis process.



**Figure 1.** (a) XRD pattern of CsPbBr<sub>3</sub> NPLs prepared at 100 °C for 60 min. (b) TEM image of the lying flat CsPbBr<sub>3</sub> NPLs prepared at 100 °C for 60 min. (c) TEM image of the perpendicularly oriented CsPbBr<sub>3</sub> NPLs. (d) Photograph of CsPbBr<sub>3</sub> NPLs dispersed in n-hexane with low concentration (left) and high concentration (right). (e) Photograph of the CsPbBr<sub>3</sub> NPLs powder prepared per single experimental run. (f) Optical absorption (UV-vis, green line), PL emission (PL, black dash line), and PL excitation (PLE, red line) spectra of the sample. (g) Time-resolved PL decay and fitting curves of the light emission at 456 nm from CsPbBr<sub>3</sub> NPLs.

by tuning the solvothermal reaction times (also see Figure S<sub>4</sub>).

It has been previously demonstrated that the CsPbBr<sub>3</sub> NPLs with a thickness relative to the exciton Bohr of CsPbBr<sub>3</sub> display strong thickness-dependent PL emission.<sup>28, 41</sup> The control of the plate thickness with various number of monolayers enables regularly PL position shift due to the strong quantum confinement. However, it is noteworthy that, in our method, it is most likely that the tunable lateral size is responsible for the red-shifted PL emission, rather than the thickness variation.<sup>39</sup> In fact, both theoretical study and experimental data have shown that, if the number of CsPbBr<sub>3</sub> monolayer increase, PL position will shift with an average distance of more than ~10 nm <sup>28, 3<sup>8, 41, 44</sup> (Manna group observed a distinct PL shift from</sup> 2.83 to 2.70 eV when the thickness of  $CsPbBr_3$  NPLs increases from 3 to 5 monolayers<sup>28</sup>). This value is much larger than the average PL shift distances observed in our samples.

To validate the hypothesis that the PL shift origins from the tunable lateral size, we further performed TEM analysis on the stacks of aligned CsPbBr<sub>3</sub> NPLs to estimate their thickness. As shown in **Figure 2k and 2**l, the NPLs are lying perpendicularly with respect to the carbon film. For the initial sample (30 min, 100 °C), the NPLs have a thickness of ~4.2 nm. Interestingly, after the reaction time was prolonged to 24 h, the thickness of the obtained CsPbBr<sub>3</sub> sample remains fixed at ~4.2 nm. It is also noteworthy that, since only a single emission peak has been observed



**Figure 2.** (a) PL emission spectra of CsPbBr<sub>3</sub> NPLs prepared at 100 °C for 30, 60, 200, 420 min and 24 h respectively. (b) UV-vis absorption (solid line) and PL emission spectra (dash line) of the different CsPbBr<sub>3</sub> NPLs. (c-f) TEM images of CsPbBr<sub>3</sub> NPLs prepared at various reaction times. (g-j) The corresponding statistical histograms on the lateral sizes of CsPbBr<sub>3</sub> NPL samples. (k) TEM image of the perpendicularly oriented CsPbBr<sub>3</sub> NPLs prepared at 100 °C for 30 min. (l) TEM image of the perpendicularly oriented CsPbBr<sub>3</sub> NPLs prepared at 100 °C for 24 h.

in the spectra, all the CsPbBr<sub>3</sub> samples should have a uniform size distribution. Therefore, by varying the solvothermal reaction times, we were able to fine-tune the lateral size of the NPLs while keeping their thickness fixed in the strong quantum confinement regime, and achieving the precise PL emission control. We also conduct a theoretical calculation to evaluate the red-shift PL of the NPLs with different sizes. Preliminary results are shown in **Figure S**<sub>5</sub>.

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It is noteworthy that the lateral sizes of CsPbBr<sub>3</sub> NPLs prepared after different solvothermal reaction times are still relative to the quantum confinement regime, which is quite different from CsPbBr<sub>3</sub> nanosheets with micrometer-sized lateral dimension reported by Manna group.<sup>39</sup> Therefore, the tunable lateral size control could lead to the precisely controlled PL emission. Unlike the hot injection method which can immediately quench the reaction by ice-water bath<sup>1, 18</sup>, the present solvothermal synthesis in the sealed environment still leads to quality NPLs with precisely tunable lateral sizes. We believe that the relatively low crystal growth rate in the solvothermal reaction plays a vital role in the size control. The low temperature and high pressure environment enable the reaction between Cs-oleate and PbBr<sub>2</sub> precursors to take place at relatively low temperatures and the kinetics of the reaction can also be depressed. As a result, CsPbBr, NPLs with tuned lateral sizes can be obtained by adjusting the reaction times. In addition, we changed the amine ligands with different carbon chains instead of OLA. No NPLs were obtained (Figure S6), indicating that the OLA ligands play an important role on the formation of CsPbBr<sub>3</sub> NPLs. During the solvothermal reaction, the OLA ligands capping on the nuclei surface promote the anisotropic NPL growth effectively. The vertical growth rate of CsPbBr, nuclei has been depressed, leading to the formation of NPLs. It is also noteworthy that, with the solvothermal time increasing, the lateral sizes of NPLs gradually change, while the vertical thickness still remains constantly. Even after long reaction for 24 h, the average size of the NPLs still remains in quantum confinement re-Therefore, gime.

#### **Chemistry of Materials**



**Figure 3.** (a) XRD patterns of various products obtained by changing the reaction conditions, showing the conversion from cubic CsPbBr<sub>3</sub> to rhombohedral Cs<sub>4</sub>PbBr<sub>6</sub> and a reversible transformation from rhombohedral Cs<sub>4</sub>PbBr<sub>6</sub> to cubic CsPbBr<sub>3</sub>. (b) UV-vis absorption (solid line) and PL emission (spherical dashed line) of Cs<sub>4</sub>PbBr<sub>6</sub> NCs (blue line) and CsPbBr<sub>3</sub> NPLs (green line). (inset) Photographs of two samples, showing distinc color change.



**Figure 4.** (a-d) TEM images of samples prepared by solvothermal reaction using increased amount of Cs-oleate precursors (2 mL, 3.5 mL, 7.0 mL and 20 mL, respectively), showing transformation from pure CsPbBr<sub>3</sub> NPLs (a) into pure Cs<sub>4</sub>PbBr<sub>6</sub> NCs (d). (e-g) TEM images of samples prepared by solvothermal reaction of the pre-synthesized Cs<sub>4</sub>PbBr<sub>6</sub> NCs with different amount of PbBr<sub>2</sub> precursor (10 mL, 20 mL and 35 mL, respectively), showing revisible transformation from Cs<sub>4</sub>PbBr<sub>6</sub> NCs to CsPbBr<sub>3</sub> NPLs. (h-j) The structural models of cubic CsPbBr<sub>3</sub> and rhombohedral Cs<sub>4</sub>PbBr<sub>6</sub>. (k-n) HRTEM images and the corresponding FFT patterns of CsPbBr<sub>3</sub> NPLs and Cs<sub>4</sub>PbBr<sub>6</sub> NCs, respectively.

the precise lateral size control can be achieved via changing the solvothermal reaction times. The reason for NPL growth with dimension variations under the particular solvothermal reactions is unkown till date and needs further investigations.

The solvothermal reaction temperature is also critical in controlling the lateral size and tuning the PL properties of CsPbBr<sub>3</sub> samples. As shown in **Figure S7-S8**, the PL emission peaks of the samples could be tuned from 450 nm to 465 nm by varying the reaction temperatures from 60 °C to 180 °C. TEM images also show the well-dispersed homogeneous NPLs have lateral size variation with the temperature increase. The gradually increase of lateral width and decrease of lateral length enables the red shift of PL emission.

Moreover, the present solvothermal method can be further extended for structure and composition control over the cesium lead halide NCs. In fact, our method enables the successful transformation of CsPbBr<sub>3</sub> NPLs to Cs<sub>4</sub>PbBr<sub>6</sub> NCs by increasing the amount of Cs-oleate precursor and the reversible transformation from Cs<sub>4</sub>PbBr<sub>6</sub> NCs to CsPbBr<sub>3</sub>NPLs through adding a certain amount of PbBr<sub>2</sub> precursor to the pre-synthesized Cs<sub>4</sub>PbBr<sub>6</sub> NCs. To the best of our knowledge, our work constitute the first report on the successful reversible structural and composition transformation between CsPbBr<sub>3</sub> NPLs and Cs<sub>4</sub>PbBr<sub>6</sub> NCs.

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In fact, herein the solvothermal growth of CsPbBr<sub>3</sub>NPLs is under Pb rich reaction conditions with an excess of PbBr<sub>2</sub> precursor.<sup>45</sup> By gradually increasing the amount of Cs-oleate precursor (from 2 mL to 20 mL), the obtained product changes from cubic CsPbBr<sub>3</sub> phase into rhombohedral Cs<sub>4</sub>PbBr<sub>6</sub> phase, as determined by XRD analysis shown in Figure 3a. After adding of 20 mL Cs-oleate precursor, the obtained product shows peaks at  $2\theta$ =12.6, 12,9, 20.1, 22.4, 25.6 and 30.5° corresponding to diffractions from {012}, {110}, {113}, {300}, {024} and {223} planes of rhombohedral Cs<sub>4</sub>PbBr<sub>6</sub> (PDF card No 73-2478). The color of the product changes from initial light green to milky white (Inset of Figure 3b). Interestingly, we also find that the Cs<sub>4</sub>PbBr<sub>6</sub> NCs can be further transformed into CsPbBr<sub>3</sub> NPLs by a post synthesis reaction with PbBr<sub>2</sub> precursor. By reacting a certain amount of PbBr<sub>2</sub> precursor with the presynthesized Cs<sub>4</sub>PbBr<sub>6</sub> NCs, the product changed into pure perovskite CsPbBr<sub>3</sub> phase completely (Figure 3a). More detailed structure transformation has been displayed in Figure S9 and supporting information.

Optical studies indicate that the transformed Cs<sub>4</sub>PbBr<sub>6</sub> NCs exhibit different absorption and PL emission peaks compared with initial CsPbBr<sub>3</sub>NPLs (Figure 3b). The UVvis characteristic absorption peak has been shifted to ~314 nm. These absorbance feature is consistent with previous experimental and theory studies on Cs<sub>4</sub>PbBr<sub>6</sub> NCs,<sup>46</sup> implying its wide bandgap. We believe that Cs<sub>4</sub>PbBr<sub>6</sub>NCs will not exhibit PL emission in the visible range because of the wide bandgap (Cs<sub>4</sub>PbBr<sub>6</sub>=3.95 eV).<sup>47</sup> The observed weak PL emission originates from minor CsPbBr<sub>3</sub> impurities mixed in the Cs<sub>4</sub>PbBr<sub>6</sub> product, even if apparently no trace of CsPbBr<sub>3</sub> phase can be found in XRD results. Since CsPbBr<sub>3</sub> displays a high PLQY, the green PL emission can be detected from only a very small trace of CsPbBr<sub>3</sub> impurities in the product. Similar opinion has also been reported by Akkerman et al.47 PL emissions of the intermediate products with mixed phases are also shown in Figure S10.

The structural and composition transformation between CsPbBr<sub>3</sub> NPLs and Cs<sub>4</sub>PbBr<sub>6</sub> NCs was further confirmed by TEM analysis. The NPLs gradually become irregular and some NCs with hexagonal shape begin to appear (**Figures 4**a-c). HRTEM images of the intermediate product are shown in **Figure S**11. Upon increasing the amount of Cs-oleate precursor to 20 mL, monodisperse Cs<sub>4</sub>PbBr<sub>6</sub> NCs with uniform hexagonal shape can be obtained (**Figure 4**d). Moreover, by post-solvothermal reaction of the pre-synthesized Cs<sub>4</sub>PbBr<sub>6</sub> NCs with different amounts of PbBr<sub>2</sub> precursor, an interesting reversible transformation from Cs<sub>4</sub>PbBr<sub>6</sub> NCs into CsPbBr<sub>3</sub> NPLs takes place (**Figures 4**d-g). Finally pure CsPbBr<sub>3</sub> NPLs with well size distribution and shape uniformity can be obtained (Figure 4g). Figures 4h-j show the structural models and phase transformation between cubic  $CsPbBr_3$  and rhombohedral  $Cs_4PbBr_6$ .

HRTEM images clearly show the well-defined CsPbBr<sub>3</sub> NPLs and hexagonal-shaped Cs<sub>4</sub>PbBr<sub>6</sub>NCs (**Figures 4**k, l), respectively. The measured *d*-spacing of 6.8 Å matches well with the {110} plane of rhombohedral Cs<sub>4</sub>PbBr<sub>6</sub>. The corresponding fast Fourier transform (FFT) patterns are show in **Figures 4**m-n. SEM image of the synthesized Cs<sub>4</sub>PbBr<sub>6</sub> NCs also displays uniform and monodisperse morphology (**Figure S12**). The large area monolayer of NCs indicates the high yield production of Cs<sub>4</sub>PbBr<sub>6</sub> NCs. The average size of the resulting Cs<sub>4</sub>PbBr<sub>6</sub> NCs is ~12.5 nm. In fact, Cs<sub>4</sub>PbBr<sub>6</sub> NCs with increased diameters can be obtained by simply prolong the solvothermal reaction time as shown in **Figure S13**.

#### CONCLUSIONS

In summary, a facile solvothermal method has been developed for the large-scale preparation of ultrathin CsPbBr<sub>3</sub> NPLs using a mixture of Cs-oleate and PbBr<sub>2</sub> precursors. Through varying the reaction temperatures and/or times, the lateral sizes of CsPbBr<sub>3</sub> NPLs can be well controlled while their thicknesses are still kept in the quantum confinement regime. Different with the thicknessdependent PL emission reported by other research groups, our method enables the fine-tuning of lateral NPL sizes, leading to more precise modulation of PL emissions. Moreover, the CsPbBr<sub>3</sub>NPLs can be converted into hexagonal-shaped Cs<sub>4</sub>PbBr<sub>6</sub> NCs by using increased amount of Cs-oleate precursor during the solvothermal reaction. Interestingly, through solvothermal reaction of PbBr, precursor with the pre-synthesized Cs<sub>4</sub>PbBr<sub>6</sub> NCs, an reversible transformation from Cs<sub>4</sub>PbBr<sub>6</sub> NCs to CsPbBr, NPLs have been achieved. The developed solvothermal method leads to the successful control over the size, structure and composition of cesium lead halide NCs, which can find widespread applications in solar cells, light-emitting diodes, photodetectors and lasers. We also envision that the synthetic approach can be easily extended to synthesis of other perovskite NCs with different halide compositions.

#### ASSOCIATED CONTENT

#### Supporting Information.

Experimental details on conditions for the various syntheses, additional data from structural analysis (HAADF-STEM, TEM, FFT, Time-resolved PL decay, SEM, XRD, UV-vis and PL spectra), theoretical calculation, additional data from statistical diagrams and optical photos. This material is available free of charge via the Internet at http://pubs.acs.org.

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