Supporting Information

Tuning the Emission Wavelength of Lead Halide Perovskite NCs via Size and Shape Control

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Scheme 1. A series of lead halide perovskite NCs were synthesized in this study. The colored frames are our original methods. The emission wavelength and FWHM of the isolated NC products are listed together with the reaction temperature in the right column. The stable emission of RGB primary colors was realized by samples C2' (red), G6 (blue) and H4 (green).

1. Material Preparation

1.1. Cs-oleate Precursor

The Cs-oleate precursor was prepared by the method reported by Pan et al. with a slight modification. First, 240 mg (1.25 mmol) of cesium acetate (Cs-OAc) and 0.65 mL of oleic acid (OA) were loaded into a 3-neck flask along with 10 mL of 1-octadecene (ODE), degassed by a mechanical pump, and stirred under vacuum at 80 °C. After approximately one hour of reaction, all solids and bubbles in the solution disappeared. When the reaction between Cs-OAc and OA was completed, a clear solution was obtained. Next, the solution temperature was increased to 120 °C, degassing was continued for another 30 min, and then, the generated acetic acid was extracted. Nitrogen gas was flowed into the reaction flask with the light-yellow colored solution at room temperature until a large amount of milky white flocculent sediment appeared. The precipitate was then redissolved by stirring at temperatures above 60 °C. This solution was used as the Ce precursor to synthesize CsPbBr3 and CsPbI3.
We use C-OAc in this reaction instead of cesium carbonate,1 because the reaction between Cs-OAc and OA is faster and thus the preparation time for precursor can be shortened. In addition, this reaction does not produce water unlike the reaction with cesium carbonate, which is preferred to keep perovskite products stable.

1.2. FA-oleate Precursor

Formamidinium (FA)-oleate precursor was prepared via a reported approach developed by Protesescu et al. with slight modification.2 First, 630 mg (6 mmol) of FA-OAc was loaded into a 3-neck flask along with 20 mL of OA, degassed by a mechanical pump and stirred under vacuum at room temperature. After one day or more of reaction, all solids and bubbles in the solution disappeared. When the reaction between FA-OAc and OA was completed, a clear light-yellow solution was obtained. Next, the solution temperature was increased to 120 °C, degassing was continued for another 30 min, and then, the generated acetic acid was extracted. Next, the solution was kept in a flask filled with nitrogen at room temperature. This solution was used without reheating as the FA precursor to synthesize FAPbBr₃.

1.3. CsPbI₃ NCs (hot injection method; Samples A and B)

First, 0.6 mL of OA, 0.5 mL of oleylamine (OLA), and 100 mg (0.217 mmol) of PbI₂ were loaded into a 50 mL size of 3-neck flask along with 5 mL of ODE, degassed by a mechanical pump, and stirred under vacuum at 60 °C until the PbI₂ salt was completely dissolved. Next, the solution temperature was increased to 120 °C, and degassing was continued for 30 min. Then, the solution temperature was increased to the target temperature (100–180 °C). When the solution temperature reached the target, 0.4 mL of prepared Cs-oleate precursor solution was quickly injected. After the reaction for 5–10 sec, the reactant was quenched in an ice-water bath. The crude product mixture was directly transferred into centrifuge tubes, and the nanocrystals (NCs) were isolated by centrifugation at 10,000 rpm for 10 min. The supernatant was removed, and the precipitated NCs were dispersed in hexane. This dispersion was purified by centrifugation at 10,000 rpm for 10 min. The precipitate was discarded, and the supernatant was kept for further use.

The key to this experimental procedure was to heat the lead iodide precursor to a state close to lead iodide salt recrystallization. Since the lead iodide precursor solution is sensitive to the temperature and heating time, first, the reaction solution was dissolved completely at a lower temperature (60 °C) and then heated (to 120 °C) and finally brought to a suitable reaction temperature. The supernatant after the first centrifugation was nearly transparent red.

1.4. CsPbI₃ NCs (modified hot injection method; Sample C)

First, 0.5 mL of OA, 0.6 mL of OLA, and 100 mg (0.217 mmol) of PbI₂ were loaded into a 50 mL size of 3-neck flask along with 5 mL of ODE, degassed by a mechanical pump, and stirred under vacuum at 60 °C until the PbI₂ salt was completely dissolved. Next, the solution temperature was increased to 150–170 °C. When the solution reached the target temperature, after waiting for another 5 min, 0.4 mL of prepared Cs-oleate precursor solution was quickly injected. After the reaction for 5–10 sec, the reactant was quenched by putting the flask into an ice-water bath. In this case, a large amount of small NCs remained in the product mixture. The supernatant after the first centrifugation was opaque and bright red. Next, a 2–3 times volume of hexane was added to the supernatant for "centrifugation of
a frozen eutectic mixture" at 10,000 rpm for 10 min to isolate small NCs. The supernatant was transparent orange-red. The supernatant was then removed, and the centrifugation was repeated until all the NCs were separated from the solution. The precipitated NCs were redispersed in hexane. This dispersion was purified one more time by centrifugation at 10,000 rpm for 10 min, the precipitate was discarded, and the supernatant was kept for further use.

1.5. CsPbI$_3$ NCs (low-temp mixing and heat-up; Sample D)

The amount of the materials and mixing ratio were the same as those of the hot injection method (see 1.3). The detailed reaction conditions are described in the results and discussion.

1.6. CsPbBr$_3$ NCs (hot injection method; Sample E)

First, 0.6 mL of OA, 0.5 mL of OLA, and 69 mg (0.188 mmol) of PbBr$_2$ were loaded into a 50 mL size of 3-neck flask along with 5 mL of ODE, degassed by a mechanical pump, and stirred under vacuum at 100–200 °C for one hour or more until the PbBr$_2$ salt was completely dissolved. Then, 0.4 mL of prepared Cs-oleate precursor solution was injected. After reacting for 5–10 sec, the reaction was quenched by placing the flask in an ice-water bath. The crude product mixture was directly transferred into centrifuge tubes, and the NCs were isolated by centrifugation at 5,000 rpm for 10 min. The supernatant was decanted, and the precipitated NCs were dispersed in hexane. This dispersion was purified by centrifugation at 10,000 rpm for 10 min, the precipitate (oversized particles and other solid impurities) was discarded, and the supernatant was kept for further use.

The key to this experimental procedure was the preparation temperature and time of the lead bromide precursor solution and the reaction temperature when the two precursors were mixed. The size of the final product was adjustable by these two parameters.

1.7. CsPbBr$_3$ NCs (modified hot injection method; Sample F)

The amount of materials and mixing ratio were the same as those of the hot injection method (see 1.6). The detailed reaction conditions are described in the results and discussion.

1.8. CsPbBr$_3$ NCs (low-temp mixing and heat-up; Sample G)

First, 1.5 mL of OA, 1.0 mL of OLA, and 160 mg (0.435 mmol) of PbBr$_2$ were loaded into a 10 mL size of round-bottom flask, degassed by a mechanical pump, and stirred under vacuum at 120 °C until the PbBr$_2$ salt completely dissolved. This lead bromide precursor was cooled to room temperature. The solution was transparent, light-yellow, and viscous. Then, 0.8 mL of Cs-oleate precursor solution was injected and stirred well at room temperature (at least 5 min). At this time, the solution became milky white opaque, with no visible fluorescence under UV light. The reaction mixture was degassed under vacuum for 5 min.

The reaction temperature and time were selected as follows to realize the thermodynamically controlled reaction: 40 °C for 120 min, 55 °C for 90 min, 70 °C for 60 min, 80 °C for 30 min, 100 °C for 15 min, and 140 °C for 15 min. After the reaction, the reaction mixture was cooled in an ice-water bath. The solution gradually turned opaque light yellow during the reaction, and visible blue fluorescence emerged under UV light. The reaction mixture was degassed under vacuum for 5 min.

The reaction temperature and time were selected as follows to realize the thermodynamically controlled reaction: 40 °C for 120 min, 55 °C for 90 min, 70 °C for 60 min, 80 °C for 30 min, 100 °C for 15 min, and 140 °C for 15 min. After the reaction, the reaction mixture was cooled in an ice-water bath. The solution gradually turned opaque light yellow during the reaction, and visible blue fluorescence emerged under UV light. The crude product mixture was directly transferred into centrifuge tubes, and the NCs were isolated by centrifugation at 10,000 rpm for 10 min. The centrifugation was repeated to remove the supernatant including the excess solvents and ligands and to
isolate the solid precipitate. The precipitated NCs were redispersed in hexane. This dispersion was purified one more time by centrifugation at 10,000 rpm for 10 min. The precipitate was discarded, and the supernatant was kept for further use.

The critical step for this reaction was to mix the two precursors (cesium and lead bromide) at room temperature and stir them until they were entirely homogeneous. If we mixed the two precursors at high temperatures, byproducts were generated, and the reaction between inhomogeneous mixtures resulted in broadened or multiple peaks in the PL spectrum.

1.9. FAPbBr$_3$ NCs (modified hot injection method; Sample H)

First, 1.0 mL of OA, 0.5 mL of OLA, and 69 mg (0.188 mmol) of PbBr$_2$ were loaded into a 50 mL size of 3-neck flask along with 5 mL of ODE, degassed by a mechanical pump, and stirred under vacuum at 160 °C for an hour or more until the PbBr$_2$ salt was completely dissolved. Next, 0.6–1.1 mL of prepared FA-oleate precursor solution was injected. After reacting for 5–10 sec, the reaction was quenched by placing the flask in an ice-water bath. The crude product mixture was directly transferred into centrifuge tubes, and NCs were isolated by centrifugation at 5,000 rpm for 10 min. The supernatant was decanted, and the precipitated NCs were dispersed in hexane. This dispersion was purified by centrifugation at 10,000 rpm for 10 min. The precipitate was discarded, and the supernatant was kept for further use.

The FA series perovskite NCs should be prepared in the presence of abundant formamidinium cations, different from the other perovskite NCs, as described in the results and discussion. Relatively uniformly sized NCs were stably obtained at reaction temperatures of 150–160 °C. To form stable NCs by this method, a large amount of OA (1.0 mL in this case) was also required. When the amount of OA was insufficient, the solution became orange-yellow and opaque during the reaction and then became transparent with no fluorescence.

2. Influence of the Reaction Temperature for Synthesis of CsPbI$_3$ NCs

![Figure S1](image)

**Figure S1.** CsPbI$_3$ reaction mixture synthesized by the conventional hot injection method at (a) 150 °C, (b) 120 °C (scale-up to 2x) and (c) 100 °C. Images were taken after the first centrifugation. The amount of products isolated by centrifugation decreased, and the color of the supernatant became more intense at reaction temperatures of 150 or 120 °C. This result indicates that small NCs could not be precipitated.
and instead remained in the solution. On the other hand, when synthesized at 110 °C or below, a large amount of NCs precipitated, and the supernatant was less colored. The reason is likely that the morphology of the products changed at this temperature, as suggested by the TEM image in Figure 1.

3. Influence of the Amount of ODE for Synthesis of CsPbI₃ NCs

![Figure S2. Influence of the amount of reaction solvent (ODE) on the PL spectra for CsPbI₃ NCs.](image)

Figure S2. Influence of the amount of reaction solvent (ODE) on the PL spectra for CsPbI₃ NCs. 0 means no addition of ODE, 1x means the amount in the original protocol, and 0.25x and 0.5x mean using a reduced amount of ODE. The detailed experimental conditions are available in the experimental section.

For the hot injection method, the solvent is not always necessary. However, when there is no proper amount of solvent, the reactant precursor becomes very viscous, which prevents uniform and thorough mixing of the Cs-oleate precursor and lead iodide precursor at the early stage of the reaction. This issue caused local crystal growth before completing nucleation, resulting in broadening of the PL spectra due to the wide size distribution of the NCs, as shown in Figure S2. On the other hand, when the amount of solvent was excessive, the yield of the final products was reduced.

The surface ligands OA and OLA play an important role in preparing precursors. When only OA is in the solution, the lead iodide salt is not dissolved. When only OLA is in the solution, the lead iodide salt is dissolved very slowly, and the product becomes unstable. Only the addition of both OA and OLA accelerates the salt dissolution process.

The lead iodide precursor solution easily reprecipitates as a lead iodide salt (yellow solid powder) at high temperature or under long-term heating conditions. Excessive OA exacerbates this situation, while excessive OLA can alleviate it. Therefore, by increasing the amount of OLA, the maximum temperature for the reaction can be increased. However, if the amount of OLA is too high, a nonluminescent white solid will be obtained instead of the luminescent product, and the synthesis will fail.

These results indicate that OLA can increase the solubility of the lead iodide salt in the precursor solution but may reduce the supersaturation and hence the chance of nucleation. This result is consistent with other perovskite NC studies.³⁴ In these studies, the synthesis without using OLA significantly lowered the threshold temperature for production. Interestingly, these phenomena are contrary to the experience of the synthesis of traditional binary compound semiconductor NCs (CdSe, ZnS, InP, etc.).
The role of amines as ligands has been discussed for the synthesis of these traditional QDs, in which ligands were believed to promote the reactivity of the precursor complex.\textsuperscript{5,8} Our results imply essential differences for the synthesis of perovskite NCs from those of traditional semiconductor NCs, which requires further investigation and verification.

4. **PL and Absorption Spectra of CsPbBr\textsubscript{3} and FAPbBr\textsubscript{3}**

![Figure S3. PL and absorption spectra of CsPbBr\textsubscript{3} (E1 and E2) and FAPbBr\textsubscript{3} (H4).](image)

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