Polar-Solvent-Free Synthesis of Highly Photoluminescent and Stable CsPbBr₃ Nanocrystals with Controlled Shape and Size by Ultrasonication

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ABSTRACT: In this work, we report a polar-solvent-free, low-cost, and environmentally friendly method for synthesizing highly stable all-inorganic CsPbBr₃ nanocrystals (NCs). Their shape and size are controlled by adjusting key parameters in the synthesis, such as capping ligands as well as ultrasound power and radiation time. The CsPbBr₃ NCs are tunable from three-dimensional to two-dimensional and finally to 0-dimensional, by controlling the ratios and types of capping ligands. The CsPbBr₃ NCs exhibit optical properties dependent on their shape and size, with photoluminescence quantum yield as high as 83%. Moreover, the role of nonpolar solvents in improving the stability of the CsPbBr₃ NCs and the mechanism for the tunable growth of CsPbBr₃ NCs are studied and discussed. Controlled shape and size of perovskite NCs are desired for applications, including solar cells, lasers, light-emitting diodes, and solar concentrators.

INTRODUCTION

Lead halide perovskites (LHPs) of the typical formula APbX₃ (A = Cs⁺, CH₃NH₃⁺, or CH(NH₂)₂⁺; X = Cl⁻, Br⁻, and I⁻) have emerged as a new potential class of optoelectronic materials because of their novel properties, such as large absorption coefficients, high charge carrier mobility, and long exciton diffusion lengths. These outstanding properties have shown them to be promising prospects of applications in light-emitting diodes (LEDs), high-efficiency solar cells, field-effect transistors, lasers, photodetectors, and memory devices. Thin-film perovskite solar cells have achieved >23% power conversion efficiency, and perovskite LEDs with external quantum efficiencies over 10%. Key to these successes is the development of various synthetic techniques to control the morphology, shape, and size of the LHPs. Tuning the dimension from the bulk to the nanoscale, the LHPs exhibit distinctive properties, including narrow emission band, high photoluminescence (PL) quantum yield (QY), broad wavelength coverage, and low trap state density. Given the dimension-dependent optical and electronic properties, a better understanding of the fundamental relationship between dimensionality and properties requires synthesis of different shapes and sizes of LHPs. Despite the fact that LHP nanocrystals (NCs) with various shapes and sizes, such as three-dimensional (3D) nanocubes, two-dimensional (2D) sheets/nanoplatelets, one-dimensional (1D) nanorods/nanowires (NWs), and 0-dimensional (0D) quantum dots (QDs), have been reported, it is desired to develop highly efficient synthesis strategies for LHP nanostructures with controlled shape and size.

To date, two classes of synthetic approach have been developed to synthesize all-inorganic CsPbX₃ NCs, namely, chemical vapor deposition (CVD) and solution chemical process. Compared to CVD, the solution chemical process, mainly including hot injection, room-temperature (RT) ligand-mediated reprecipitation, and RT supersaturated recrystallization (SR) process, has advantages of facile processing, low cost, and control over size, morphology, and shape. The widely adopted approach for preparing CsPbX₃ NCs with high PL QY is based on hot injection, which was proposed by Kovalenko and co-workers in 2015, and developed by Alivisatos et al. to achieve nanoplatelets. However, high temperature, inert atmosphere, and vacuum environment are required for the hot injection approach, which will greatly increase cost and result in low reproducibility. Toward this issue, several RT synthesis strategies were developed, involving a ligand-assisted reprecipitation that allows for shape control. Additionally, an RT SR method...
was used to prepare CsPbX₃ NCs, which can be obtained within a few seconds. However, RT methods were processed by mixing a precursor solution in the polar solvent (such as N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO)) with a large amount of nonpolar solvent (such as toluene and n-hexane), whereas the CsPbX₃ NCs are found to be very sensitive to polar solvents. The commonly used polar solvents, such as DMF or DMSO, result in defects in CsPbX₃ NCs. In addition, DMF, DMSO, toluene, and n-hexane are toxic and not environmentally friendly.

At present, one of the major issues facing LHP NCs is their instability toward polar solvents, oxygen, heat, and UV light illumination, which limits their practical applications. A common approach for improving LHP stability is surface modification and passivation, including modifying with hydrophobic molecules, integrating/coating with polymers/metal oxides, and doping perovskites with dopant ions (e.g., Mn²⁺), to enhance energy of formation. Another strategy for stabilizing LHPs is to use nonpolar solvents (e.g., 1-octadecene) to prevent oxygen and moisture from reaching the core ionic crystal. Whereas some methods have been reported for synthesizing LHP NCs without using polar solvents, they do not allow control over shape and size.

Besides product quality, cost is also an important factor for practical applications. One potential strategy for large-scale synthesis with low cost is to simplify the process of the one-pot reaction. Ultrasonication-assisted synthesis, as a promising method to quickly achieve high-quality particles, has been widely used to synthesize various nanomaterials, such as graphene, carbon nanotubes, semiconductors, metal, and metal oxide nanoparticles. This method has been recently employed by Feldmann et al. and Rogach et al. for the synthesis of perovskite NCs, demonstrating the potentials for ultrasonication-assisted synthesis of high-quality CsPbX₃ NCs. Different from the common hot injection method, the ultrasonication-assisted reaction proceeded in an open environment, during which the precursors and solvents were not pretreated and degassed. It will not only drive the nucleation and growth of high-quality NCs but also reduces energy consumption and time. To date, however, little attention has been paid to analyze in detail the effects of ultrasonication on the shape and size of perovskite.

In this work, we address the above issues by introducing ultrasonication and nontoxic and polar-free-solvent liquid paraffin to synthesize CsPbBr₃ NCs with desired shape and size in a one-pot reaction. This method avoids the use of any polar solvent and uses minimum toxic solvent (such as toluene and n-hexane) compared to RT synthesis strategies. Furthermore, it avoids multiple dissolution and reprecipitation and can significantly reduce the synthesis time, effort, and thereby the production cost. The optimized CsPbBr₃ NCs show a high PL QY of up to 83%. By tuning the ratios and thereby the production cost, the optimized CsPbBr₃ NCs can signifi- cantly reduce the synthesis time, e

ter the formation of CsPbBr₃ NCs with desired shapes and sizes are investigated.
Characterization of the CsPbBr3 nanocubes. The PL QYs of the CsPbBr3 NCs were calculated by utilizing the following equation:

\[
Q = \frac{Q_x}{Q_{st}} \times \frac{n_x}{n_{st}}
\]

where \(Q\) is the QY, and the subscripts \(x\) and \(st\) represent the sample and standard, respectively. Quinine sulfate (the QY is 0.55) is used as the standard for LHP NCs. \(K\) is the slope determined by the ratio of the linear curves of the integrated fluorescence intensity to absorbance. \(n\) is the refractive index of the solvent.

RESULTS AND DISCUSSION

Characterization of CsPbBr3 Nanocubes. We first synthesized CsPbBr3 nanocubes by adding 0.5 mL of OA and 0.5 mL of OAm in the liquid paraffin and then the mixture was processed by tip-sonication at a power of 90 W for 40 min. TEM was performed to characterize the crystal structure and surface morphology of as-prepared CsPbBr3 NCs. Figure 1a shows the forming of CsPbBr3 nanocubes with quasicubic structure in the current reaction systems. The HRTEM image in Figure 1b displays lattice fringes with an interplanar spacing of 5.7 Å, corresponding to the (100) crystal plane of bulk CsPbBr3, which is consistent with the JCPDS PDF #18-0364 or the Inorganic Crystal Structure Database (ICSD) Collection Code #97851. Figure 1c demonstrates that the typical CsPbBr3 nanocubes have a narrow size distribution with an average diameter of ~14.9 nm. Furthermore, the EDX spectrum confirmed that the CsPbBr3 nanocubes consisted of Cs, Pb, and Br elements (Figure S3). In order to determine the phase structure, XRD was used to characterize the as-prepared samples. As shown in Figure 1d, the main peaks of XRD pattern at 2θ = 15.2°, 21.5°, 26.5°, 30.4°, 30.7°, 34.3°, 37.6°, 43.7°, and 46.6° coincide with the diffractions pattern from 218paraffin, 0.60 mL of OA, and 0.40 mL of OAm. Then, the reaction medium was processed by tip-sonication at a power of 120 W (40% of the total power) for 20 min. After completion of the reaction, unreacted precursors and excess ligands were removed by centrifugation at a speed of 10 000 rpm for 10 min and then the precipitate was redispersed in 5.0 mL of n-hexane. Then, the solution was centrifuged at a speed of 12 000 rpm for 5 min and the sediment was redissolved in toluene or n-hexane for further characterization. We utilized 260 P Br2 (0.30 mmol) and CsBr (0.30 mmol) were loaded in DMF (10 mL). OAm (0.50 mL) and OA (0.50 mL) were added to stabilize the precursor solution. Then, 1.0 mL of the precursor solution was quickly dropped in toluene (10 mL) with intense stirring. The centrifugation process was same as that of the nanocubes. The procedure followed by Zeng’s group reported, \(CsPbBr3\) NCs were synthesized CsPbBr3 nanocubes by adding 0.5 mL of OA and 0.5 mL of OAm in the liquid paraﬁn and then the mixture was processed by tip-sonication at a power of 90 W for 40 min. Then, the solution was processed by tip-sonication at a power of 90 W for 40 min. The UV−vis absorption spectra (red line) and PL emission spectra (blue line). Inset is a representative digital photograph under 365 nm UV light irradiation. (f) Contour plot of the colored PL intensity measured as a function of excitation wavelength with CsPbBr3 nanocubes.
Relative humidity is 70%. Figure 2a shows the photostability of CsPbBr₃ nanocubes in toluene without any protective layer. These nanocubes are found to be very sensitive to these polar solvents. The DMF used in the SR synthesis process, where the CsPbBr₃ nanoparticles obtained displayed superior stability as compared with SR. This is mainly ascribed to the lack of any disruptive polar solvents, such as DMSO or DMF, used in the SR synthesis process, where the CsPbBr₃ nanocubes have a highly homogeneous surface structure and a narrow size distribution, consistent with TEM results. Additionally, the CsPbBr₃ nanocubes have a small Stokes shift (~15 nm) between the first excitonic absorption peak and the PL emission peak, which coincides with a direct exciton recombination process. The PL QY was calculated to be 83% by using eq 1, as presented in Table S1. The contour plot (Figure 1f) of the PL emission and PL excitation spectra of CsPbBr₃ nanocubes shows the strongest emission centered at 520 nm when excited at different excitation wavelengths (400–500 nm). The observed contour demonstrates that the CsPbBr₃ nanocubes have an exciton-independent emission behavior, implying that the CsPbBr₃ nanocubes have a highly homogeneous surface structure and a narrow size distribution, consistent with TEM results.

The photostability and thermostability of the as-prepared CsPbBr₃ nanocubes synthesized by ultrasonication in this study have been compared with the same CsPbBr₃ nanocubes prepared by the RT SR (as presented in the Experimental Section). Two kinds of LHP NCs disperse in toluene without any further protection in the air environment and the mean relative humidity is 70%. Figure 2a shows the photostability of these two different CsPbBr₃ nanocubes under a 365 nm UV excitation for up to 3000 s. For CsPbBr₃ nanocubes fabricated by the SR approach, the PL intensity declines fast within 200 s and remains at approximately 57% of its original value after 3000 s of the 365 nm UV light illumination. Surprisingly, the PL intensity of CsPbBr₃ nanocubes prepared by ultrasonication reduces slowly and remained at 86% after 3000 s of UV light illumination, showing superior stability as compared with SR. This is mainly ascribed to the lack of any disruptive polar solvent, such as DMSO or DMF, used in the SR synthesis process, where the CsPbBr₃ NCs are found to be very sensitive to these polar solvents. The main cause of the instability of LHP NCs is the deprotonation reaction between nucleophilic solvent molecules and protoligands of amino ligands. As a consequence, the amino ligands will drop off the surface of LHP NCs, which are subsequently decomposed by polar solvents. In addition, the thermostability of these two CsPbBr₃ nanocubes' film under 80 °C heating was further studied. The PL intensity of CsPbBr₃ nanocubes synthesized by SR reduced quickly within 30 min, and the PL emission signal almost disappeared after 150 min, as shown in Figure 2b. The CsPbBr₃ nanocubes synthesized by ultrasonication proved to be much more stable than SR-synthesized LHP NCs, as indicated by their slower decrease in PL intensity and remained at around 80% of their original value after 150 min. Furthermore, we evaluated the chemical stability of CsPbBr₃ nanocubes at different protic and polar solvents, including methanol, water, ethanol, and isopropanol. As shown in Figure S4a, the relative PL intensity of the CsPbBr₃ nanocubes remained at 67% for ultrasonication and at 5% for SR after 2 h of being dispersed in isopropanol. Moreover, Figure S4b–d shows that the CsPbBr₃ nanocubes synthesized by ultrasonication are also more stable than SR-prepared nanocubes. These results indicate that the CsPbBr₃ nanocubes synthesized by ultrasonication have a much higher stability than SR because of the assistance of nonpolar liquid paraffin.

The above results demonstrate that the substitution of polar solvent (DMF or DMSO) by liquid paraffin greatly improved the stability of CsPbBr₃ nanocubes. There are two possible explanations as shown in Scheme 2. First, the liquid paraffin, as a hydrophobic substance, can prevent moisture and oxygen from getting incorporated into the intrinsic ionic crystal structure during the synthesis process; (b) Liquid Paraffin Protects Halogen Hydrogen-Bonding from Being Broken Because of Free Oxygen

![Figure 2](image-url)
362 time on the properties of CsPbBr₃ NCs. Figure 3a,b shows the 363 times (200 min). The UV–vis absorption peak owing to the 364 CsPbBr₃ NCs that were synthesized at different ultrasound 365 power, and capping ligands, determine the 366 para- to avoid breaking [Br−N−H⁺] hydrogen-bonding interactions, as 367 the ligands on CsPbBr₃ nanocubes surface are highly dynamic. 368 In addition, the strength of the [Br−N−H⁺] hydrogen- 369 bonding interaction is weaker compared to metal–ligand 370 coordination, which is further subdued in water or other polar 371 solvents. As shown in Figure S4, the use of polar solvents, 372 such as DMF, methanol, water, ethanol, and isopropanol, 373 unsettles the [Br−N−H⁺] hydrogen-bonding interaction and 374 separates the ammonium ions from the surface. Liquid para- 375 fin acting as the non-coordinating solvent, whose molecular 376 formula can be expressed as R−(CH₂)ₙ−CH₃ (16 ≤ n ≤ 20), is readily oxidized to be more stable R−CH═CH−(CH₂)ₙ−CH₃ with two H atoms dehydrogenated under 377 ultrasonic stimulation, and these H atoms can interact with 378 oxygen to avoid breaking [Br−N−H⁺] hydrogen-bonding and 379 even supply H⁺ for protonation reaction. Therefore, liquid 380 paraffin stabilizes the CsPbBr₃ NCs.

381 The synthesis conditions, such as ultrasound time and 382 power, and capping ligands, determine the final size, 383 morphology, shape, and optical properties of the LHP NCs. 384 We first investigated the effects of ultrasound 385 time on the properties of CsPbBr₃ NCs. Figure 3a,b shows the 386 change of UV–vis absorption spectra and PL spectra of 387 CsPbBr₃ NCs that were synthesized at different ultrasound 388 times (2–100 min). The UV–vis absorption spectra in Figure 3a 389 first red shift and then blue shift as the ultrasound time increases from 2 to 100 min, which is possibly related to the 390 change of surface state and size of LHP NCs. At the beginning of the reaction (2–20 min), the size of the LHP NCs increases with increasing ultrasound time, whereas the effective band gap decreases and the corresponding absorption spectra red shifts. As time increases (20–100 min), in spite of the size of the LHP NCs continuing to increase, which would be further confirmed by TEM, a blue shift in the absorption peak owing to the carboxylates and ammonium ions binding to the NC surface results in an increase in the strength of the bond. Meanwhile, the normalized PL spectra in Figure 3b gradually red shift because of the size of LHP NCs increasing with increasing ultrasound time.

391 TEM was applied to monitor the change on morphology and 392 size of CsPbBr₃ NCs. Figure 3c–f shows the representative 393 TEM images of CsPbBr₃ NCs that were synthesized at 5, 20, 394 50, and 80 min, respectively. At 5 min, the TEM image shows a 395 mainly amorphous structure, indicating no LHP NCs formed. 396 With the ultrasound time increasing, the well-defined and 397 monodispersed CsPbBr₃ NCs were achieved and their size 398 increased significantly (Figure 3d–f). Therefore, the size of the 399 LHP NCs can be tuned by controlling the ultrasound time and 400 result in a corresponding PL spectral shift. We further 401 investigated the relationship between band gap energy and 402 the corresponding size of CsPbBr₃ NCs by collecting the data 403 from previous reports as shown in Figure 3g. It is 404 demonstrated that the band gap energy of CsPbBr₃ NCs depends on their size. We found that the relationship between band gap energy and size of CsPbBr₃ NCs in this work is 405 consistent with fitting in Figure 3g (the data fitted by the 406 effective mass approximation theory, which is expressed by a 407 1/r² function, where r represents the size of the LHP NCs), 408 suggesting that the CsPbBr₃ NCs PL spectral shift is mainly 409 due to size effect. Stokes shift was further measured between 410 the PL emission peak and the absorption band edge, as shown 411 in Figure 3h. The Stokes shift decreases gradually to a 412 minimum value at an ultrasound time of 25 min, followed by 413 an increase at a longer time. When the ultrasound time was 414 <25 min, the Stokes shift reduced gradually because of the size 415 effect, consistent with previous reports. However, as the 416 ultrasound time was >25 min, Stokes shift increased, which is 417 possibly due to nonradiative recombination of excitons 418 dominance over size effect as a result of exciton–phonon 419 interaction.

420 Moreover, we also investigated the effect of ultrasound 421 power on the properties of CsPbBr₃ NCs. Figure 5a,b shows 422 that when the ultrasound power is ≤60 W, very weak PL 423 intensity was detected, indicating there was almost no LHP 424 NCs formed. When the ultrasound power was >60 W, with 425 increasing ultrasound power, both the UV–vis absorption and 426 PL spectra red shifted. Such red shifts occur either because of 427 the higher energy light emitted by a smaller NC is reabsorbed 428 by a larger NC with a smaller optical band gap, and/or the 429 excited smaller NC nonradiatively transfers its energy to a 430 larger NC. Meanwhile, the absorption spectra have a sharp 431 valley (509 nm) and peak (527 nm) when the ultrasound 432 power was 180 W, suggesting that too high an ultrasound 433 power can change the structure of perovskites (Figure S6 and 434 Table S3). Additionally, the signal for longer wavelengths 435 increased with ultrasound power, which is indicative of increased scattering because of the presence of larger crystals 436 in the dispersion. The Stokes shift increases with the increase 437

![Figure 3](image-url)
of ultrasound power, as shown in Figure S5c. In terms of colloidal NCs, Stokes shift results from phonon-assisted emission, band-edge fine-structure splitting, and size polydispersity, or a combined effect of them.58 Compared with single CsPbBr3 NCs, the bigger Stokes shift in CsPbBr3 NCs possibly arises from their broader size distribution. As shown in Figure S6, the size polydispersity becomes more and more obvious. However, large size polydispersity results in fluorescence quenching as high energy photons emitted by smaller NCs were probably reabsorbed by larger NCs, thereby leading to a decrease of PL QY. The PL QY increased gradually to a maximum value at an ultrasound power of 120 W, followed by a decline at a higher power, as shown in Figure S5d. Therefore, the highest PL QY was reached with the optimum ultrasound power of 120 W.

**Characterization of CsPbBr3 Nanoplatelets.** We adjusted the ratio of OA and OAm, ultrasound power, and irradiation time, while maintaining other synthesis conditions same as those of CsPbBr3 nanocubes. With 0.2 mL of OA and 0.8 mL of OAm, and 120 W of ultrasound power applied for...
Figure 6. Characterization of the CsPbBr₃ QDs. (a) TEM image. (b) HRTEM image. (c) Size distribution. (d) XRD patterns. Black lines and red lines represent experimental data and standard reference, respectively. (e) Optical absorption spectra (red line) and PL emission spectra (blue line). Inset is a representative digital photograph under 365 nm UV irradiation. (f) Graphical depictions of the colored PL intensity measured as a function of excitation wavelength with CsPbBr₃ QDs’ colloidal solution.

Characterization of CsPbBr₃ NWs. The synthesis of CsPbBr₃ NWs was carried out by replacing OA with EA with ultrasound power and irradiation time at 120 W and 30 min, respectively. Figure 5a–c shows the typical TEM and HRTEM images of CsPbBr₃ NWs and their size distribution. The CsPbBr₃ NWs have a length of >1 μm and a diameter of ~11 nm. The HRTEM image shown in Figure 5b clearly exhibits a d-spacing of 5.6 Å corresponding to the (100) crystal face. Upon changing the amounts of EA, different morphologies and sizes of CsPbBr₃ NCs were obtained, as shown in Figure S8 and Table S4, which indicate 1D NWs were formed by the oriented attachment with the assistance of organic ligands. Figure Sd shows the XRD pattern with peaks at 2θ = 15.1°, 21.7°, 30.4°, 30.7°, 37.6°, and 43.6°, corresponding to diffraction patterns from the (100), (110), (002), (200), (121), and (202) crystal planes of bulk orthorhombic CsPbBr₃. The XRD data verified the forming of CsPbBr₃ NWs with a space group Pbnm (62), which corresponds to the JCPDS PDF #18-0364. In addition, weak peaks in the XRD pattern suggest that some rhombohedral Cs₄PbBr₆ (JCPDS PDF #73-2478) were formed. The first excitonic absorption peak of the CsPbBr₃ NWs is at approximately 493 nm and the PL emission peak is at about 503 nm with a narrow FWHM of 18 nm, as shown in Figure 5c. Figure 5f shows the PL image calculated as a function of excitation wavelength (280–480 nm) for the CsPbBr₃ NWs. This result demonstrates that the emission range coincides with the change of excitation wavelength, suggesting uniform CsPbBr₃ NWs.

Characterization of CsPbBr₃ QDs. Upon changing the ratio of OA to OA−m to 0.60 and 0.40 mL and decreasing the ultrasound time to 20 min, we obtained monodispersed CsPbBr₃ QDs. Figure 6a,b demonstrates the TEM and HRTEM images of CsPbBr₃ QDs with an interplanar distance of 3.3 Å, which is in accord with the (111) crystal plane of the orthorhombic CsPbBr₃ bulk crystal. Figure 6c indicates the CsPbBr₃ QDs have uniform size distribution with an average diameter of 3.9 nm. To further analyze the crystal structure, XRD was applied, as shown in Figure 6d, and reveals peaks at 2θ = 15.1°, 21.5°, 30.4°, 30.7°, 34.2°, and 37.6°, complying with diffractions of the (100), (110), (002), (200), (121), and (202) planes of orthorhombic CsPbBr₃, corresponding to...
Comparing with the standard XRD PDF card, very small parts of rhombohedral Cs$_4$PbBr$_6$ and PbBr$_2$ (JCPDS PDF #73-2478, 31-0679) were found, demonstrating this reaction not completely. The UV-vis absorption spectra and PL emission spectra of CsPbBr$_3$ QDs show the first characteristic absorption peak of about 482 nm and the PL emission of around 493 nm with a narrow fwhm of 16 nm, as displayed in Figure 6e. Furthermore, the small Stokes shift (11 nm) indicates the PL emission of CsPbBr$_3$ QDs results from the bound exciton recombination. The PL QY was estimated to be $\sim$58% (see Table S1), lower than those of CsPbBr$_3$ nanocubes and nanoplatelets, possibly due to increased OA concentration leading to formation of non-fluorescent bulk LHP NCs from smaller QDs. The PL images characterized as a function of excitation wavelength for the QDs are presented in Figure 6f.

Furthermore, we studied the effect of other ratios of OA and OAm on the properties of CsPbBr$_3$ NCs. For example, morphology changes of CsPbBr$_3$ NCs at different ratios of OA and OAm were shown in Figure S9 and Table S5, demonstrating that this approach can be used to make Cs$_4$PbBr$_6$ NCs with tunable shape and size. Compared to the TEM images of different CsPbBr$_3$ NCs, we can draw some significant conclusions. On the one hand, no fluorescent LHP NCs were produced when no OA or OAm was used as coordinating ligands in the reaction system (Figure S9a,b), indicating that different morphologies can be obtained only in the presence of both OA and OAm. On the other hand, increasing the OAm amount can slow down the growth rate of the LHP NCs, whereas an excess amount stops the nucleation process (Figure S9c−f). Besides, much excessive OAm will result in the forming of CsPbBr$_3$ NCs derivative Cs$_4$PbBr$_6$, which will cause fluorescence quenching of LHP NCs (Figure S9g−i). All the above results show that the ammonium ions are effective for regulating the anisotropic growth of the LHP NCs, whereas carboxylate ions are more effective in manipulating the size of the LHP NCs.

**Scheme 3. Formation Mechanism of CsPbBr$_3$ NCs with Different Shapes and Sizes with Ligand Assistance**

There are two possible stages in the growth processes of the four distinct kinds of LHP NCs: micelle formation and oriented growth. 3D CsPbBr$_3$ nanocubes were achieved with equal OA and OAm, and 2D nanoplatelets could be obtained with relatively more OAm used. With an increase in OA, the 3D nanocubes would be changed into 0D QDs. By replacing OA with EA, 1D NWs could be obtained.

Formation Mechanism of CsPbBr$_3$ NCs with Different Shapes and Sizes. The above results demonstrate that 3D CsPbBr$_3$ nanocubes were achieved with equal OA and OAm, and 2D nanoplatelets could be obtained with relatively more OAm used. With an increase in OA, the 3D nanocubes would be changed into 0D QDs. These represent the fact that the shape of the as-synthesized LHP NCs could be tailored from 3D to 2D and finally to 0D, by controlling the ratios and types of capping ligands. Such shape-change is mainly ascribed to the micellar transition and growth kinetics, where the organic ligands are selectively attached to the given facets via electrostatic and hydrophobic interaction, resulting in the different growth rates in various crystal facets. There are two possible stages in the growth processes of the four distinct kinds of LHP NCs, as illustrated in Scheme 3. At the initial stage, the ligands play the role of generating micelles for the perovskite precursors, and react quickly (within 10 min) to form a turbid dispersion, as shown in Figure S2, named as micelle formation. After that, the dispersion followed a prolonged ultrasonic processing, during which the ligands...

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preferentially absorb with particular crystal facets to form various shapes, known as oriented growth.

The shape-change with the variation of OA and OA or EA confirms that the ammonium ions are effective for tuning the anisotropic growth of the LHP NCs, whereas carboxylate ions are more effective in regulating the size of the LHP NCs. When equal OA and OAm or more OA were added, both of them act synergistically, which favors the micelle isotropic growth.

Increasing the amounts of OAm, the excess OAm selectively binds with (001) crystal faces of CsPbBr$_3$ NCs and inhibits their vertical oligomerization. Therefore, the formation rates of (001) crystal facets are much slower than that of (100) and (110) crystal facets (as XRD shown in Figure 4e), which form 2D nanoplatelets. A similar situation has been observed in previous reports. The EA is readily decomposed into acetic acid (AA) and ethanol (EtOH) with continuous ultrasonic treatment. As OA is replaced by EA, it can remove some OAm from the bound surface of the LHP where small NCs can attach easily, which can lead to an oriented growth of the LHP NCs, thereby forming some nanorods (Figure 5a). Moreover, hydrophobic, hydrocarbon-terminated groups of AA between adjacent LHP NCs are situated closely via electrostatic interaction. Therefore, the final 1D NWs could be formed through the oriented attachment of these small NCs and nanorods. The XRD in Figure 5d and TEM images in Figure S8 confirmed the formation of 1D NWs via oriented attachment along with (200) facet with the assistance of OAm and EA.

CONCLUSIONS

In summary, we have demonstrated a fast, low-cost, environmentally friendly, and polar-solvent-free strategy using ultrasonication for synthesizing all-inorganic CsPbBr$_3$ NCs with tunable shape and size. Changing the ratio of OA and OAm, 3D nanocubes, 2D nanoplatelets, and 0D QDs can be obtained, whereas replacing OA with EA results in 1D NWs, 3D nanocubes, 2D nanoplatelets, and 0D QDs can be obtained, whereas replacing OA with EA results in 1D NWs. Meanwhile, the sizes of the CsPbBr$_3$ NCs could be tuned by controlling the ultrasound power and reaction time. The optical band gap and emission wavelength of the CsPbBr$_3$ NCs are tunable by varying shape and size. Moreover, by taking advantage of liquid paraffin, the photo-, thermo-, and chemical stabilities of the LHP NCs are significantly enhanced compared to the LHP NCs prepared by the RT SR method. This is attributed to the ability of liquid paraffin in preventing moisture and oxygen from reaching the crystal core structure and breaking [Br$^-$–H$^+$] hydrogen-bonding during the synthesis process. Additionally, mechanistic studies reveal that the shape change is related to micellar transition and growth kinetics, where ammonium ions are effective for tuning the anisotropic growth of the LHP NCs and carboxylate ions are more efficient in regulating the size of the LHP NCs. This work provides valuable insights into the mechanism growth of different dimensional LHP NCs with high stability and desired optical properties potentially useful for optoelectronic applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.8b03298.

Photographs of ultrasound machine and reaction medium; EDX spectrum; additional UV–vis absorption and PL spectra; TEM images; AFM image; PL QY of samples; morphology change of CsPbBr$_3$ NCs at different ultrasound times, different ultrasound powers, different amounts of EA, and different ratios of OA and OAm (PDF).


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