Aqueous Phase Exfoliating Quasi-2D CsPbBr₃ Nanosheets with Ultrahigh Intrinsic Water Stability

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All-inorganic cesium lead halide perovskite nanocrystals (NCs) have emerged as attractive optoelectronic materials due to the excellent optical and electronic properties. However, their environmental stability, especially in the presence of water, is still a significant challenge for their further commercialization. Here, ultrahigh intrinsically water-stable all-inorganic quasi-2D CsPbBr₃ nanosheets (NSs) via aqueous phase exfoliation method are reported. Compared to conventional perovskite NCs, these unique quasi-2D CsPbBr₃ nanosheets present an outstanding long-term water stability with 87% photoluminescence (PL) intensity remaining after 168 h under water conditions. Moreover, the photoluminescence quantum yields (PLQY) of quasi-2D CsPbBr₃ NSs is up to 82.3%, and these quasi-2D CsPbBr₃ NSs also present good photostability of keeping 85% PL intensity after 2 h under 365 nm UV light. Evidently, such quasi-2D perovskite NSs will open up a new way to investigate the intrinsic stability of all-inorganic perovskites and further promote the commercial development of perovskite-based optoelectronic and photovoltaic devices.
Herein, we present the ultrahigh intrinsically water-stable all-inorganic quasi-2D CsPbBr$_3$ nanosheets (NSs) via employing a facile aqueous phase exfoliation method. Due to the protection of OH group, along with enhanced formation energy and suppressed ion migration of such unique quasi-2D CsPbBr$_3$ NSs, their degradation in water can be obviously inhibited. It results in an outstanding long-term water stability with remaining 87% photoluminescence (PL) intensity after 168 h under water condition. Moreover, the photoluminescence quantum yields (PLQY) of quasi-2D CsPbBr$_3$ NSs is up to 82.3%, and they also present good photostability with keeping 85% PL intensity after 2 h under 365 nm UV light. Therefore, we believe that these unique quasi-2D perovskite NSs will provide a potential path to deeply investigate the all-inorganic intrinsic stability perovskite materials and further promote the commercial development of perovskite-based optoelectronic and photovoltaic devices.

Due to the inherent ionic character, the lead-halide perovskite NCs will decompose fast in the present of water or other polar solvent. However, in this study, we make a crazy attempt to synthesize stable quasi-2D all-inorganic perovskite NSs in water by aqueous phase exfoliation method. The schematic illustration of the aqueous phase exfoliation process has been shown in Figure 1a. At first, we take full advantage of the water-triggered transformation from Cs$_4$PbBr$_6$ to CsPbBr$_3$[9] to get CsPbBr$_3$ crystal in water. Then, there may be a process of water molecules intercalation that caused by the osmotic pressure.[10] Finally, quasi-2D CsPbBr$_3$ NSs with highly intrinsic water stability are prepared in water.

Figure 1b–e shows the scanning electron microscopy (SEM) images of Cs$_4$PbBr$_6$ and CsPbBr$_3$ in different stages of aqueous phase exfoliation. These changes of micro-morphology intuitively demonstrate the evolution process of aqueous phase exfoliation. In Figure 1b, the sizes of rhombohedral Cs$_4$PbBr$_6$ NCs are about 100–200 nm and has no luminescent before immersing in water. Once dispersed into water, this intrinsically unstable rhombohedral Cs$_4$PbBr$_6$ NCs will be quickly broken and decomposed into Cs$^+$ and PbBr$_6^{4-}$ ions. And then, these free ions tend to recrystallize into large CsPbBr$_3$ particles with the help of CsPbBr$_3$ seed crystals.[11] Then, CsPbBr$_3$ crystals may be dissolved by forming step-like etch pits[12] as shown in Figure 1d. And this etch pits cause damage that let water have the chance to intercalate into CsPbBr$_3$ crystals layer by layer. Finally, under the osmotic pressure of solvent, the large CsPbBr$_3$ crystals exfoliate into more stable quasi-2D CsPbBr$_3$ NSs (Figure 1e).
This aqueous phase exfoliation process may be further illustrated by the X-ray diffraction (XRD) results of different stages (Figure 1f). From which, there is only Cs₄PbBr₆ (JCPDS CARD NO. 73–2478) NCs at the start of aqueous phase exfoliation (Figure 1f, #1). After 2 min (Figure 1f, #2), there are some new diffraction peaks that can be indexed as CsPbBr₃ (JCPDS CARD NO. 18–0364). After 4 h, there only exist the characteristic peaks of CsPbBr₃ (Figure 1f, #3), obviously presenting the complete phase transition from Cs₄PbBr₆ to CsPbBr₃. Finally, there are only two obvious preferential peaks (Figure 1f, #4) at 15.2° and 30.7° in the XRD spectra, which correspond to (100) and (200) planes that both belong to {100} planes family of CsPbBr₃ respectively. XRD result and SEM image (Figure 1e) evidently reveal that the final product is quasi-2D CsPbBr₃ NSs.[13] And these preferential peaks adequately show the excellent crystallization of as-prepared quasi-2D CsPbBr₃ NSs, which is in favor of its intrinsic stability in water. The successful synthesis of all-inorganic quasi-2D perovskite in water should open a new door for improving the intrinsic stability of all-inorganic perovskite in environment.

Figure S2a in the Supporting Information have shown the typical transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images of Cs₄PbBr₆ NCs. From Figure S2a in the Supporting Information, Cs₄PbBr₆ NCs have the unique rhombohedral morphology with sizes of 100–200 nm, which are in good agreement with that of Figure 1b. Further, its high resolution TEM (HRTEM) image (Figure S2b, Supporting Information) obviously presents the excellent crystallization property, and the interplanar distances of 0.39 nm corresponding to the (300) crystal plane can evidently demonstrate rhombohedral phase Cs₄PbBr₆, which also agrees well with the XRD result (Figure 1f, #1). To further characterize Cs₄PbBr₆ NCs' optical properties, the UV–vis absorption and PL emission spectra of Cs₄PbBr₆ NCs' toluene solution have shown in Figure S2c in the Supporting Information. The Cs₄PbBr₆ NCs have a sharp absorption at 312 nm, which can be also proved from the characteristic absorption peak of the previous report.[11] In addition, the intense PL emission peak at 334 nm come from the emission of Cs₄PbBr₆ NCs, while the weak peak at 510 nm stem from CsPbBr₃ because of the unavoidable coexistence with Cs₄PbBr₆.

After aqueous phase exfoliation, we successfully obtain water-stable quasi-2D CsPbBr₃ NSs (Figure 2a) from rhombohedral Cs₄PbBr₆ NCs. From the typical TEM image and HRTEM image (Figure 2b) of these quasi-2D CsPbBr₃ NSs, they obviously show good crystallinity, and their interplanar distances of 0.29 nm corresponding to the (200) crystal plane can be easily identified. Furthermore, the HRTEM image also confirms there is no water resistant shell like Pb(OH)₂[14] coated on the NSs surface, which further proves that the water stability of these quasi-2D CsPbBr₃ NSs should result from this unique 2D morphology and their excellent crystallization. Besides, the atomic force microscopy (AFM) was used to evaluate the thickness of these quasi-2D CsPbBr₃ NSs. A representative AFM topography image is reported in Figure 2c. The different colors in the image correspond to different heights. From the height profiles (Figure 2cii,iii), we estimated an 8 nm thickness for a single NSs. It is noteworthy that the sizes of quasi-2D NSs in AFM and TEM

![Figure 2. Characterization of quasi-2D CsPbBr₃ NSs synthesized by aqueous phase exfoliation. a) SEM image, b) TEM image and HRTEM image of quasi-2D CsPbBr₃ NSs, c) AFM image and the height profiles of the quasi-2D CsPbBr₃ NSs, and d) absorption and PL spectra of quasi-2D CsPbBr₃ NSs.](image-url)
images are smaller than those in the SEM image, which may arise from the fracture of the quasi-2D NSs caused by intense ultrasound in sample preparation. According to Figure 2d, the first absorption peak of quasi-2D CsPbBr\(_3\) NSs aqueous solution is around 518 nm, while its PL emission peak is located at 523 nm. Because of quantum confinement effect (QCE),\([15]\) there is a slight blue-shift of PL emission peak compared to its bulk material.\([16]\) This aqueous solution will show bright green fluorescence when irradiated by UV light (Figure S3d, Supporting Information), and its PLQY is remarkably as high as 82.3% for the completely water-dispersed lead-halide perovskites.\([17]\)

For the deep understanding of the evolution process from Cs\(_4\)PbBr\(_6\) NCs to quasi-2D CsPbBr\(_3\) NSs, we recorded the emission spectra of different reaction time (Figure 3a). It can be obviously found that a weak emission peak will appear at first two minutes and continually increase with the immersion time. This increase of PL intensity correspond well with the phenomenon in Figure S3 in the Supporting Information, and its PLQY is remarkably as high as 82.3% for the completely water-dispersed lead-halide perovskites.\([17]\)

\[ I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \]  

where \(I(t)\) is time-dependent PL intensity. \(\tau_1\) and \(\tau_2\) denote short-lived and long-lived decay lifetime, which correspond to the nonradiative recombination stemming from the trap-state and the radiative recombination of intrinsic exciton respectively.\([19]\) The \(A_1\) and \(A_2\) constants can represent the proportion of each component. In addition, the average lifetime can be obtained by Formula 2. These as-fitted parameters and the corresponding analysis results were shown in Table 1.

Figure 3b presents PL decay curves of the samples at the different reaction time of 2 min, 20 min, 4 h, and 24 h. As a result, its average lifetime increases rapidly from 45.77 to 78.47 ns in the first four hours (the detailed values are shown in Table 1), which mainly depend on the grain growth of CsPbBr\(_3\).\([20]\) It confirmed the continuous transformation from non-luminescent Cs\(_4\)PbBr\(_6\) to luminescent CsPbBr\(_3\) again. More interestingly, although this transformation has completely finished after 4 h (XRD patterns of Figure 1e), the PL intensity still greatly increases from 4 to 24 h. This interesting result should be rooted from the gradual surface defects decrease of CsPbBr\(_3\) crystals. In this process, water plays a key role to dissolve the excessive ions of CsPbBr\(_3\) crystal surface to remove their surface defects,\([21]\) which also can be further confirmed by the fitting results time-resolve PL decay curves (Figure 3d). From it, the long-lived decay lifetime rate (\(\tau_2\%\)) increase from 64.14% to 92.84% while the short-time lifetime rate (\(\tau_1\%\)) reduced from 35.86% to 7.16%.

![Figure 3. The PL spectra, time-resolved PL decay and their analysis results of different time in water. a) The PL spectra, b) time-resolved PL decay and fitting curves of Cs\(_4\)PbBr\(_6\) NCs immersed in water after 2 min, 20 min, 1 h, and 24 h. c) Time-resolved PL decay and fitting curves of Cs\(_4\)PbBr\(_6\) NCs immersed in water after 24, 48, and 72 h. d) The relative percentage of \(\tau_1\) and \(\tau_2\).](image-url)
35.86% to 7.16% in the first day, evidently revealing the decrease of surface defects that cause nonradiative recombination.[22]

While in Figure 3c, time-resolved PL decay and fitting curves of 24, 48, and 72 h show the gradual reduce of the average lifetime with increasing reaction time (Table 1), which should be mainly ascribed to the exfoliation from bulk-like CsPbBr3 crystals to quasi-2D CsPbBr3 nanosheets.[10b,23] In addition, this reduced-dimension exfoliation will introduce a large number of surface defects with the increase of the specific surface area, leading to the increase of nonradiative recombination ratio. As shown in Figure 3d, the visibly increasing of short-lived lifetime (τ1) at 48 h evidently demonstrates the water-assisted exfoliation process of bulk-like CsPbBr3 NCs. Compared with other samples, its short-lived lifetime (τ1) also increases significantly (Table 1), which further proving the increasing of surface state because the decay lifetime of surface-state emission is longer than trap-state emission. [19a] Moreover, this exfoliation will increase the solution concentration, so the PL intensity can keep continuous enhancement (Figure 3a). Then, water will promptly remove or passivate the surface defects on the newly generated surface of quasi-2D CsPbBr3 NSs, resulting in the ultrahigh intrinsically water-stable all-inorganic quasi-2D CsPbBr3 NSs. [22b] Therefore, this decreasing surface defect will cause the rise of the long-lived decay lifetime ratio (τ2/τ1) again (Figure 3d). Moreover, energy dispersive spectrometer (EDS) results (Figures S4 and S5, Supporting Information) demonstrate the approximate atomic ratio of Pb:Br = 1:3 for CsPbBr3 crystals while that of Pb:Br = 1:3:8 for quasi-2D CsPbBr3 NSs, obviously indicating a Br-rich surface of the quasi-2D CsPbBr3 NSs. These abundant Br anions at perovskite surface will connect with the adjacent cations and then inhibit the trapping of excited electrons by surface defects, effectively promoting the increase of PL intensity.[24]

To assess the water stability of quasi-2D CsPbBr3 NSs, we directly dispersed the quasi-2D CsPbBr3 NSs into water to monitor their PL spectra at different immersion time (Figure 4a). For comparison, we prepared CsPbBr3 QDs by conventional room-temperature supersaturated recrystallization method.[19a] These conventional CsPbBr3 QDs were dissolved in toluene and placed on the top of water and saturated CsBr salt aqueous solution (maximizing the contribution of CsBr to water stability) respectively, and corresponding temporal evolution process of PL spectra were shown in Figure 4b and Figure S6 in the Supporting Information. Obviously, CsPbBr3 NCs are very sensitive to water and has a fast PL quenching to 3% of initial PL intensity only after few hours (Figure 4c the blue line and the green line). Conversely, the as-prepared quasi-2D CsPbBr3 NSs possess an outstanding water stability of around 87% remaining (Figure 4c, the red line) and well keep crystal structure (Figure S7, Supporting Information) after 168 h immersed in water. From the inset of Figure 4c, it is apparent the extra CsBr salt in water will delay disintegration of CsPbBr3 QDs.[17] There may be same contribution in the aqueous of quasi-2D CsPbBr3 NSs because of the stripping of CsBr in the transition from CsPbBr3 to CsPbBr3.[13] Besides, the low specific surface area of quasi-2D NSs also lead better water resistance than QDs. However, considering that the quasi-2D NSs directly contact with water while CsPbBr3 QDs are only invaded by a small amount of water molecules that diffuse into toluene, there should be more important reasons for this ultrahigh water stability. To figure out the deeper cause of the supernormal stability of the quasi-2D CsPbBr3 NSs, the Fourier transform infrared (FTIR) spectroscopy of quasi-2D CsPbBr3 NSs and CsPbBr3 QDs were recorded. In Figure S8 in the Supporting Information, the FTIR peaks around 1450, 1700, and 2800 cm−1 should belong to the stretching vibrations of C=O, C=C, and C−H, respectively. All of these peaks are attributed to attachment of OA and OAm. Besides, the peaks at 3400 cm−1 is ascribed to the OH stretching vibration. By analyzing the FTIR, the inherent differences between quasi-2D CsPbBr3 NSs and CsPbBr3 QDs are the increase of OH groups and the decrease of OA and OAm. There the OH group may replace OA and OAm as the surface ligand[25] and enhance the stability of quasi-2D CsPbBr3 NSs.[26] In other hand, the enhancement of formation energy[27] and inhibition of ions migration[28] in 2D perovskite materials may also help maintenance of quasi-2D CsPbBr3 NSs.

Table 1. Summary of time-resolved PL biexponential fitting parameters of different samples corresponding to Figure 3a,b.

<table>
<thead>
<tr>
<th>Sample</th>
<th>A1</th>
<th>t1</th>
<th>A2</th>
<th>t2</th>
<th>τave</th>
<th>τex</th>
<th>τ1 [%]</th>
<th>τ2 [%]</th>
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<tr>
<td>2 min</td>
<td>1261.99</td>
<td>4.48</td>
<td>2257.32</td>
<td>47.92</td>
<td>45.77</td>
<td>35.86</td>
<td>64.14</td>
<td></td>
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<tr>
<td>20 min</td>
<td>784.41</td>
<td>6.24</td>
<td>2444.33</td>
<td>66.51</td>
<td>64.74</td>
<td>24.29</td>
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<tr>
<td>4 h</td>
<td>402.10</td>
<td>5.72</td>
<td>2489.70</td>
<td>79.31</td>
<td>78.47</td>
<td>13.90</td>
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<tr>
<td>24 h</td>
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<td>7.01</td>
<td>2577.19</td>
<td>76.22</td>
<td>75.74</td>
<td>7.16</td>
<td>92.84</td>
<td></td>
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<tr>
<td>48 h</td>
<td>509.04</td>
<td>16.55</td>
<td>3038.01</td>
<td>70.96</td>
<td>68.92</td>
<td>14.35</td>
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<tr>
<td>72 h</td>
<td>223.32</td>
<td>7.02</td>
<td>3230.35</td>
<td>56.54</td>
<td>56.12</td>
<td>6.47</td>
<td>93.53</td>
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Figure 4. Water-stability tests of quasi-2D CsPbBr₃ NSs and CsPbBr₃ QDs. a) Temporal evolution of PL spectra of quasi-2D CsPbBr₃ NSs keep in water. b) Temporal evolution PL spectra of CsPbBr₃ QDs dispersed in toluene that place on the top of water. c) Normalized PL intensity as a function of time (QDs#1: CsPbBr₃ QDs on water; QDs#2: CsPbBr₃ QDs on saturated CsBr salt aqueous). d) The photographs of quasi-2D CsPbBr₃ aqueous under daylight (left, 0 h; right, after 168 h) and UV light (0, 24, 48, 72, 96, 120, 144, and 168 h). e) The photographs of CsPbBr₃ QDs (the top layer is toluene, the bottom layer is water) under daylight (left, 0 min; right, after 120 min) and UV light (0, 20, 60, and 120 min).

Figure 5. Photostability test of quasi-2D CsPbBr₃ and CsPbBr₃ NCs. a) Temporal evolution of PL spectra of quasi-2D CsPbBr₃ aqueous and b) CsPbBr₃ NCs’ toluene solution under irradiation. c) Emission peak position as a function of time. The insets show the color change of quasi-2D CsPbBr₃ aqueous (left) and CsPbBr₃ NC’s toluene solution (right). d) Normalized PL intensity as a function of time.
excellent intrinsic water stability. These quasi-2D CsPbBr$_3$ NSs can remain 87% PL intensity after 168 h under water condition. Moreover, the photoluminescence quantum yields (PLQY) of quasi-2D NSs is up to 82.3% and it also presents good photo-stability. We believe our finding provides a new strategy to improve the intrinsic water stability of all inorganic perovskites and play an important role for the green synthesis of lead halide perovskite in non-toxic polar solvent (eg water and ethanol).

**Experimental Section**

**Materials:** Cesium bromide (CsBr, 99.5%), lead bromide (PbBr$_2$, 99.0%), oleylamine (OLA, 80–90%), and oleic acid (OA, 90%) were purchased from Aladdin. N,N-dimethyformamide (DMF, 99.9%), toluene (99.8%) and ethanol were purchased from Kelong. Ultrapure water was made in the lab by Smart-515. All the used chemicals were without further purification.

**Synthesis of Quasi-2D CsPbBr$_3$ NSs with Aqueous Phase Exfoliation:** All synthesis were performed in air and without any pre-dried chemicals or solvents. In a typical synthesis of quasi-2D CsPbBr$_3$ NSs, CsBr (1.2 mmol) and PbBr$_2$ (0.4 mmol) were dissolved in DMF (10 mL) at room temperature (RT). OA (0.5 mL) and OLA (0.5 mL) were added into the solution and stirred for a few hours to obtain the precursor solution. Then, the cleared precursor solution was removed into a new vial, and the toluene was slowly dropped into it (volume ratio 1:1) to get nonluminous Cs$_4$PbBr$_6$ NCs precipitation. These Cs$_4$PbBr$_6$ precipitation were collected by centrifugation and further freeze-dried. Then, these Cs$_4$PbBr$_6$ NCs were put in a vial, added 15 mL ultrapure water and dispersed the Cs$_4$PbBr$_6$ powder by ultrasonic treatment. The quasi-2D CsPbBr$_3$ NSs can be obtained after 72 h.

**Preparation of CsPbBr$_3$ Nanocrystals through Supersaturated Recrystallization Method:** The synthetic method has been reported before. In a typical synthesis of CsPbBr$_3$, CsBr (0.4 mmol) and PbBr$_2$ (0.4 mmol) were dissolved in DMF (10 mL) at room temperature (RT). OA (1.0 mL) and OLA (0.5 mL) were added to stabilize the precursor solution. Then, 1 mL precursor solution was quickly added into toluene (10 mL) to induce the crystallization of via vigorous stirring. Strong green emission will be observed immediately after the injection.

**Characterization:** The scanning electron microscope (SEM) images were taken using FEI QUANTA FEG 250. X-ray diffraction (XRD) patterns in this paper were acquired using a Bruker D8 Advance X diffractometer (Cu K$_\alpha$: $\lambda = 1.5406$ Å). The crystal structure and grain size were determined by TEM (FEI Tecnai G2 F20) with acceleration voltage of 200 KV. Fluorescence emission spectra of the samples were measured using Edinburgh FLS980. The UV absorption spectrum were obtained by UV-2500 (Shimadzu Corporation). Decay times were obtained with a Xenon flash lamp as a light source at room temperature (FLS 980).

**Supporting Information**

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

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

all-inorganic perovskites, aqueous phase exfoliation, CsPbBr$_3$, intrinsic water stability, quasi-2D

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