Improving the Stability of $\alpha$-CsPbI$_3$ Nanocrystals in Extreme Conditions Facilitated by Mn$^{2+}$ Doping

Yu Ji, Jian-Bin Zhang, Hao-Ran Shen, Zhai Su, Hao Cui, Tao Lan, Jia-Qian Wang, Yu-Hui Chen, Lihui Liu, Kun Cao, Wei Shen*, and Shufen Chen*

ABSTRACT: The wide application of CsPbI$_3$ nanocrystals (NCs) is limited due to their poor phase stability. We reported that Mn$^{2+}$-CsPbI$_3$ NCs have better optical performance and phase stability. With a suitable Mn/Pb ratio (5.0%), Mn$^{2+}$-doped $\alpha$-CsPbI$_3$ NCs exhibited the best stability under UV irradiation, ethanol addition, and heating. Under UV irradiation and addition of ethanol, photoluminescence (PL) intensities of CsPbI$_3$ NCs could be only preserved up to 35% (22 min UV irradiation) and 10% (ethanol addition), respectively, whereas, Mn$^{2+}$-doped CsPbI$_3$ (5.0%) exhibited much improved stability, and their intensities could be preserved up to 70% (22 min UV) and 58% (ethanol), respectively. It should be noted that crystal-phase stability could be maintained at least 7 h even at 120 °C. We believe that the improved stability in extreme conditions for $\alpha$-CsPbI$_3$ NCs can be further applied to optoelectronic devices.

1. INTRODUCTION

All-inorganic cesium halide perovskites (ABX$_3$, A site: Cs$^+$, B site: Pb$^{2+}$, X site: Cl$^-$, Br$^-$ or I$^-$) nanocrystals (NCs) have attracted wide attention in the fields of solar cells, light-emitting diodes (LEDs), and lasers due to their unique optical properties, such as high photoluminescence quantum yield (PLQY), high color gamut, and a tunable band gap. Generally, their optical properties are directly dependent on their crystal phase. Therefore, the stability of their crystal phase is quite sensitive to their optical performance, especially for CsPbI$_3$. Cubic-phase CsPbI$_3$ ($\alpha$-CsPbI$_3$, $E_g$ = 1.73 eV) having good optoelectronic performance can be easily transformed to an orthorhombic phase ($\delta$-CsPbI$_3$, $E_g$ = 2.25 eV) with poor optoelectronic properties. The small-sized Cs$^+$ ions cannot maintain the cubic framework of a corner-sharing octahedron, which leads to phase transformation. To solve this issue, many methods have been used to stabilize $\alpha$-CsPbI$_3$, such as A$_x$ B$_y$ or X-site doping. It should be noted that B-site doping can improve the crystal-phase stability of CsPbI$_3$ without any side effects, such as ionic migration, phase separation, or photodecomposition. Rogach et al. used SrCl$_2$ as a coprecursor to improve the phase stability of $\alpha$-CsPbI$_3$ NC solutions after 60 days. Additionally, Sr$^{2+}$-ion doping and surface Cl$^-$-ion passivation could further enhance their PLQY to 84%. Yao et al. reported novel Sr$^{2+}$ doping with an I$^-$-ion passivation strategy to stabilize $\alpha$-CsPbI$_3$ quantum dots. Their PLQY can be maintained above 80% after 60 days and the phase stability of the film is for more than 20 days. Angelis et al. used MnI$_2$ to directly synthesize CsPb$_3$Mn$_{1-x}$I$_3$ NCs. Their films and solutions are stable for at least 30 days. Nag et al. doped MnI$_2$ via postsynthesis to stabilize $\alpha$-CsPbI$_3$ NCs, which exhibited good stability in ambient conditions for a month. In summary, B-site doping can improve the optical properties and crystal-phase stability of $\alpha$-CsPbI$_3$ NCs in ambient conditions, and it has the potential to expand the conditions in extreme conditions, such as ultraviolet (UV), polar solvents, and high temperature.
We believe that the improved stability in extreme conditions for α-CsPbI₃ NCs can be further applied to optoelectronic devices.

2. RESULTS AND DISCUSSION

2.1. Optical Properties. Mn²⁺-doped CsPbI₃ NCs were synthesized by a hot injection method (see the Section 4 and Figure 1).

Their UV–vis absorption spectra (Figure 2a) showed less effect after Mn²⁺ doping, which implied that Mn²⁺ cannot influence the CsPbI₃ band gap. More interestingly, the peak positions of PL show blue shifts from 685 to 679 nm (Figure 2b and Table S1). Because of the small size of Mn²⁺ partly replacing Pb²⁺, a possible lattice shrinking of CsPbI₃ NCs leads to a blue shift of their PL peaks. According to the previous studies, using a small-sized ion to replace Pb²⁺ may lead to lattice contraction and a decrease in size. The size of Mn²⁺ is 0.067 nm, which is much smaller than the size of Pb²⁺ (0.119 nm). As a result, Mn²⁺ doping in CsPbI₃ NCs leads to a blue shift of their PL spectra due to lattice contraction and size shrinking (Figure S1). To quantitatively compare the PL performance of these samples, absolute PLQYs of samples were measured. The results showed that with an increase in the Mn/Pb ratio, PLQY increased from 90...
to 98% (Figure 2c). Furthermore, PL lifetimes were measured by time-resolved PL decay curves (Figure 1d). The PL decay curves were fitted with a biexponential function (Table 1) to calculate the lifetimes of the fast components (corresponding to the nonradiative recombination/\( \tau_{nr} \)), slow components (radiative recombination/\( \tau_f \)), the radiation decay rate (\( k_r \)), and the nonradiation decay rate (\( k_{nr} \)). Compared with CsPbI\(_3\) NCs, the average PL lifetimes of Mn\(^{2+}\)-doped CsPbI\(_3\) NCs increased from 10.18 to 15.12 ns (Table 1). Both \( k_r \) and \( k_{nr} \) decreased, but \( \tau_{nr} \) decreased faster than \( \tau_f \) (Table 2). These results demonstrate that Mn\(^{2+}\) doping can effectively decrease defects and enhance PLQY.

### 2.2. Structural Characterization

According to PL spectra, Mn\(^{2+}\) doping in CsPbI\(_3\) NCs can be indirectly demonstrated. To directly confirm Mn\(^{2+}\) doping, structural and elemental characterization studies were performed via X-ray diffraction (XRD) and transmission electron microscopy (TEM). In Figure 3a, two main diffraction peaks located at 14.00 and 28.59° correspond to the (100) and (200) planes of \( \alpha \)-CsPbI\(_3\) perovskite (PDF # 97-018-1288) NCs. With an increase in the Mn/Pb ratio, both main diffraction peaks slightly shift to higher angles, especially at 28.59° (Figure 3b). This phenomenon is mainly due to the lattice contraction, which is attributed to the partial substitution of Pb\(^{2+}\) by the small-sized Mn\(^{2+}\).

In addition to the demonstration of Mn\(^{2+}\) doping by XRD data at a macroscopic level, TEM was also used to confirm such doping at a microscopic level. As shown in Figure S1, the average sizes of CsPbI\(_3\) NCs and Mn\(^{2+}\)-doped CsPbI\(_3\) NCs (Mn/Pb = 0, 0.8, 3.1, and 5.0%) are 11.39 ± 0.90, 10.80 ± 0.68, 10.20 ± 0.73, and 9.70 ± 1.4 nm, respectively. The small-sized NCs after Mn\(^{2+}\) doping mainly result in lattice contraction and the dynamics of nucleation and growth process.\(^{23,24,28}\)

Additionally, high-resolution TEM (HRTEM) images were used to identify their precise lattice distances. According to the insets in Figure 3c, the lattice distance of CsPbI\(_3\) NCs is 0.310 nm, corresponding to the (200) plane of \( \alpha \)-CsPbI\(_3\). After Mn\(^{2+}\) doping, the lattice distance of the (200) plane decreases to 0.302 nm, which is attributed to the small-sized Mn\(^{2+}\) substituting Pb\(^{2+}\). According to the XRD test results and Scherer’s formula, the crystal plane spacings of (200) are 0.311 nm (0%), 0.310 nm (0.8%), 0.310 nm (3.1%), and 0.309 nm (5.0%). The tendency of lattice contraction can be confirmed by both XRD and HRTEM. Furthermore, elemental mapping images and element contents were measured using an energy-dispersive spectrometer (EDS). Elemental analyses confirm that Mn\(^{2+}\) is doped in a CsPbI\(_3\) perovskite crystal lattice and the actual Mn doping contents are 0, 0.8, 3.1, and 5.0% for Mn/Pb from 0 to 60% (Figure S2 and Table S2). We chose the elemental mapping area of Mn\(^{2+}\)-doped CsPbI\(_3\) NCs in high-angle annular dark-field scanning transmission electron microscopy image (HAADF-STEM) (Figure 3d). On the basis of elemental mapping images (Figure 3e–h), all of the elements are uniformly distributed in NCs, and the mapping of the Mn element can be clearly observed. Therefore, these results confirm that Mn\(^{2+}\) can be successfully doped in CsPbI\(_3\) NCs.

### 2.3. PL Stability

It should be noted that Mn\(^{2+}\)-doped CsPbI\(_3\) NCs exhibited good PL stability in a long term. After being preserved in air for 36 days, PL intensity decayed less than 10% (Mn/Pb = 5.0%), while the PL intensity of CsPbI\(_3\) decayed more than 25% (Figure S3). Therefore, Mn\(^{2+}\)-doped CsPbI\(_3\) NCs showed potential to improve stability in extreme conditions. To evaluate the stability of samples, UV, polar solvent, and thermal resistance of NCs were systematically studied. First, the stability under UV irradiation (365 nm (8 W) and 254 nm (8 W)) was measured. With increasing UV irradiation time, PL intensities of Mn\(^{2+}\)-doped CsPbI\(_3\) NCs decreased. It should be noted that CsPbI\(_3\) NCs exhibited the poorest UV resistance. With the increase in illumination time, the PL intensity quickly decreased (Figure 4a). While doping Mn\(^{2+}\), their UV resistance can be dramatically improved (Figure 4b–d). Figure 4e presents the images of all samples after 22 min of UV irradiation. It is hard to observe an obvious red emission for samples of Mn/Pb = 0 and 0.8% after 22 min of UV irradiation, whereas the brightness of Mn\(^{2+}\)-doped CsPbI\(_3\) NCs (Mn/Pb = 3.1 and 5.0%) can be still observed. According to the stability decay curves (Figure 3e), the PL intensity of Mn\(^{2+}\)-doped CsPbI\(_3\) NCs (Mn/Pb = 5.0%) only decreased to 70% of the initial one after 22 min of UV irradiation, whereas PL intensity of CsPbI\(_3\) NCs decreased to 35% of the initial one in the same condition. These results demonstrated that the UV resistance of CsPbI\(_3\) NCs can be improved by Mn\(^{2+}\) doping.

It is well known that polar solvents can easily induce \( \alpha \)-CsPbI\(_3\) NC transformation to an orthorhombic phase, which results in poor PL performance.\(^{31}\) To characterize their phase stability in polar solvents, a certain amount of ethanol was added to NC solutions, and their PL intensities were used to
indirectly identify their phase stability.\textsuperscript{32,33} The results (Figures S4 and 4a) show that PL intensities for all of the samples quickly decreased after adding ethanol, and gradually tended to be stable. However, with increasing Mn\textsuperscript{2+} doping, the preserved PL intensities can be increased. The Mn\textsuperscript{2+}-doped CsPbI\textsubscript{3} NCs (Mn/Pb = 5.0\%) showed the most stability against ethanol, and 58\% PL intensity could be preserved. Therefore, PL stability can be greatly improved with addition of ethanol as compared to CsPbI\textsubscript{3} NCs (10\% PL intensity).

Furthermore, the thermal resistance of Mn\textsuperscript{2+}-doped CsPbI\textsubscript{3} NCs was studied based on their PL evolution (Figures S5 and 4b). At 80 °C, the preserved PL intensities of samples enhanced with increasing Mn/Pb ratios, and the half-lifetimes for their PL intensities (Mn/Pb = 0, 0.8, 3.1, and 5.0\%) are 19, 30, 40, and 50 min, respectively.

Figure 3. (a) XRD patterns of Mn\textsuperscript{2+}-doped CsPbI\textsubscript{3} NCs. (b) Fine XRD patterns in the region of 27–31° (Mn/Pb = 0, 0.8, 3.1, 5.0\%). (c) TEM images of CsPbI\textsubscript{3} NCs and Mn\textsuperscript{2+}-doped CsPbI\textsubscript{3} NCs. Insets: HRTEM images. (d) HAADF-STEM images of Mn\textsuperscript{2+}-doped CsPbI\textsubscript{3} NCs and the corresponding elemental mapping of Cs (e), Pb (f), Mn (g), and I (h). (c, d) Mn/Pb = 0 and 5.0\%.

Figure 4. (a–d) Evolution of PL of Mn\textsuperscript{2+}-doped CsPbI\textsubscript{3} NCs under 365 nm (8 W) and 254 nm (8 W) UV irradiation. (e) Mn\textsuperscript{2+}-doped CsPbI\textsubscript{3} NCs under 365 nm UV irradiation at 0 and 22 min. (f) Evolution of PL areas with increasing irradiation time. (a) Mn/Pb = 0\%, (b) Mn/Pb = 0.8\%, (c) Mn/Pb = 3.1\%, and (d) Mn/Pb = 5.0\%. UV resistances of NCs were observed using 365 nm (8 W) and 254 nm (8 W) UV-light sources, and their PL data were collected using an RF600 spectrofluorometer with the excitation wavelength at 500 nm.
20.5, 30, and 35 min, respectively. It should be emphasized that the decrease of PL at high temperatures may mainly result in ionic migration and crystal fusion.\textsuperscript{12,34,35} Therefore, the precise characterization of phase stability was carried out by XRD.

2.4. Crystal-Phase Stability. We further verified the thermal stability of Mn\textsuperscript{2+}-doped CsPbI\textsubscript{3} films. All of the films were placed on a hot plate at 120\textdegree C, and we periodically measured their XRD patterns. Figure 5 shows that all of the as-prepared samples exhibit a cubic phase of CsPbI\textsubscript{3}. CsPbI\textsubscript{3} films exhibited the poorest phase stability, and gradually converted from the cubic phase to an orthorhombic phase after heating at 120\textdegree C for 1 h. With increasing the Mn/Pb ratio to 0.8–3.1\%, their cubic phase can be maintained for at least 5 h. On further increasing the Mn/Pb ratio to 5.0\%, their cubic phase was stable even after 7 h. We also monitored the PL intensities of the solid film evolution at 120\textdegree C. With increasing time, PL intensities of the films decreased, and PL peaks exhibited a red shift of about 2–5 nm (Figure S6), which might be related to the growth of CsPbI\textsubscript{3} NCs due to the ionic migration, crystal fusion, and exciton quenching.\textsuperscript{12,35} Therefore, the thermal stability of CsPbI\textsubscript{3} films can be enhanced via Mn\textsuperscript{2+} doping (Figure 6).

3. CONCLUSIONS

In this work, we used Mn(Ac)\textsubscript{2} as a dopant precursor via a direct synthesis method to improve the phase stability of α-CsPbI\textsubscript{3} NCs. Mn\textsuperscript{2+} doping can dramatically decrease the defects of α-CsPbI\textsubscript{3} NCs and enhance their PLQYs. Benefiting from the suitable Mn/Pb ratio (5.0\%), their phase stabilities in extreme conditions can be further improved. Under UV irradiation and addition of ethanol, the PL intensities of CsPbI\textsubscript{3} NCs could only be preserved up to 35\% (22 min UV irradiation) and 10\% (ethanol addition), respectively, whereas Mn\textsuperscript{2+}-doped CsPbI\textsubscript{3} (5.0\%) exhibited much improved stability, and their intensities could be preserved up to 70\% (22 min UV irradiation) and 58\% (ethanol addition), respectively. Furthermore, the phase stability could be maintained for at
4. EXPERIMENTAL SECTION

4.1. Chemical Materials. Oleic acid (OA, 90%), 1-octadecene (ODE, 90%), oleylamine (OLA, 80–90%), cesium carbonate (Cs2CO3, 99.99%), manganese acetate (Mn (Ac)2, 95%), and PbI2 (99.99%) were purchased from Aladdin. All of the chemicals were used without further purification.

4.2. Synthesis of Cs-OA. Cs2CO3 (0.39 g), OA (2.0 mL), and ODE (18.0 mL) were mixed into a 100 mL three-neck flask. After degassing and drying under vacuum for 1 h at 120 °C, the solution was heated at 150 °C under N2. After a clear solution was obtained, the solution was cooled to 60 °C to obtain a Cs-OA solution.

4.3. Synthesis of OLA-HI. Twenty milliliters of OLA and 2 mL of HI were mixed into a 100 mL three-neck flask. Then, the solution was heated at 120 °C for 2 h under N2 to remove water. The solution was then cooled to 60 °C to obtain an OLA-HI solution.

4.4. Synthesis of Mn2+-Doped CsPbI3 NCs. Mn2+-doped CsPbI3 NCs were synthesized by the following method. In a typical synthesis, different ratios of PbI2 (0.4 mmol)/Mn(Ac)2 were mixed with 10 mL of ODE in a 100 mL three-neck flask, and the mixture was degassed and dried in vacuum for 1 h at 120 °C. Then, 1.0 mL of OLA, OA, and preheated OLA-HI was injected into the reaction flask, respectively. The mixed solution became clear and was degassed in vacuum for 30 min at 120 °C. Then, the temperature was increased to 260 °C. One milliliter of Cs-OA was swiftly injected. The reaction was stopped at 1 min by moving into an ice bath. The purification process was carried out twice using methyl acetate to precipitate Mn2+-doped CsPbI3 NC.

4.5. Characterization. The UV−vis absorption spectra of NC solutions were carried out using a PerkinElmer Lambda 650 S spectrophotometer. PL spectra were collected using an RF6000 spectrophotometer with an excitation wavelength of 425 nm. The crystal structures of NCs were analyzed by X-ray diffraction (XRD, Germany, Bruker X-ray diffractometer). The operation voltage and current were 40 kV and 40 mA, respectively, with Cu Kα radiation (λ = 1.5418 Å). The morphology and size of NCs were measured using a transmission electron microscope (TEM) (Hitachi, HT7700) and a high-resolution TEM (HRTEM) (Talos, F200X).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01383.

Particle size of Mn2+-doped CsPbI3 NCs, the EDX spectrum of Mn2+-doped CsPbI3 NCs, the PL spectra of Mn2+-doped CsPbI3 NCs in air, the PL spectra of Mn2+-doped CsPbI3 NCs at different times with addition of 20% ethanol, the PL spectra of Mn2+-doped CsPbI3 NCs at 80 °C, the PL spectra of Mn2+-doped CsPbI3 NCs films at different times under 120°C, the fluorescence peak position and FWHM, and the EDS analysis of Mn2+-doped CsPbI3 NCs with different nominal feeding molar ratios of Mn(Ac)2 to PbI2 during the synthesis (PDF)
Yu-Hui Chen — Key Laboratory for Organic Electronics and Information Displays & Jiangsu Key Laboratory for Biosensors, Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications (NUPT), Nanjing 210023, P. R. China

Lihui Liu — Key Laboratory for Organic Electronics and Information Displays & Jiangsu Key Laboratory for Biosensors, Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications (NUPT), Nanjing 210023, P. R. China

Kun Cao — Key Laboratory for Organic Electronics and Information Displays & Jiangsu Key Laboratory for Biosensors, Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications (NUPT), Nanjing 210023, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c01383

Author Contributions
Y.J. and J.-B.Z. contributed equally to this work.

Notes
The authors declare no competing financial interest.

Acknowledgments
This work was supported by the National Major Fundamental Research Program of China (Grant No. 91833006), the National Key Research and Development Program of China (Grant No. 2017YFB0404501), the National Science Foundation of Jiangsu Province (Grant No. BM2012010), the Priority Academic Program Development of Jiangsu Higher Education Institutions (Grant No. YX130003), and NUPTSF (Grant Nos. NY219158 and NY220025).

References
(1) Huang, H.; Bodnarchuk, M. J.; Kershaw, S. V.; Kovalenko, M. V.; Rogach, A. L. Lead Halide Perovskite Nanocrystals in the Research Spotlight: Stability and Defect Tolerance. ACS Energy Lett. 2017, 2, 2071–2083.
(2) Liu, F.; Zhang, Y.; Ding, C.; Kobayashi, S.; Iizishi, T.; Nakazawa, N.; Toyoda, T.; Ohta, T.; Hayase, S.; Minemoto, T.; Yoshino, K.; Dai, S.; Shen, Q. Highly Luminescent Phase-Stable CsPbl3 Perovskite Quantum Dots Achieving Near 100% Absolute Photoluminescence Quantum Yield. ACS Nano 2017, 11, 10373–10383.
(3) Zhang, X.; Wang, C.; Zhang, Y.; Zhang, X.; Wang, S.; Lu, M.; Cui, H.; Kershaw, S. V.; Yu, W. W.; Rogach, A. L. Bright Orange Electroluminescence from Lead-Free Two-Dimensional Perovskites. ACS Energy Lett. 2019, 4, 242–248.
(4) Dutta, A.; Behera, R. K.; Pal, P.; Baitalik, S.; Pradhan, N. Near-Unity Photoluminescence Quantum Efficiency for All CsPbl3 (X = Cl, Br, and I) Perovskite Nanocrystals: A Generic Synthesis Approach. Angew. Chem., Int. Ed. 2019, 58, 5552–5556.
(5) Jung, E. H.; Chen, B.; Bertens, K.; Vafaei, M.; Teale, S.; Propp, A.; Hou, Y.; Zhu, T.; Zheng, C.; Sargent, E. H. Bifunctional Surface Engineering on SnO2 Reduces Energy Loss in Perovskite Solar Cells. ACS Energy Lett. 2020, 5, 2796–2801.
(6) Kirmani, A. R.; Luther, J. M.; Abolhasani, M.; Amassian, A. Colloidal Quantum Dot Photovoltaics: Current Progress and Path to Gigawatt Scale Enabled by Smart Manufacturing. ACS Energy Lett. 2020, 5, 3069–3100.
(7) Han, D.; Imram, M.; Zhang, M.; Chang, S.; Wu, X. G.; Zhang, X.; Tang, J.; Wang, M.; Ali, S.; Li, X.; Yu, G.; Han, J.; Wang, L.; Zou, B.; Zhong, H. Efficient Light-Emitting Diodes Based on in Situ Fabricated FAPbBr3 Nanocrystals: The Enhancing Role of the Ligand-Assisted Recrystallization Process. ACS Nano 2018, 12, 8808–8816.
(8) Proteescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbl3; X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. Nano Lett. 2015, 15, 3692–3696.
(9) Wang, C.; Chesman, A. S. R.; Yin, W.; Frazer, L.; Funston, A. M.; Jasienska, J. J. Facile purification of CsPbl3 (X = Cl(–), Br(–), I(–)) perovskite nanocrystals. J. Chem. Phys. 2019, 151, No. 121105.
(10) Paul, S.; Bladt, E.; Richter, A. F.; Doblinger, M.; Tong, Y.; Huang, H.; Dey, A.; Bals, S.; Deb Nath, T.; Polavarapu, L.; Feldmann, J. Manganese-Doping-Induced Quantum Confinement within Host Perovskite Nanocrystals through Ruddlesden-Popper Defects. Angew. Chem., Int. Ed. 2020, 59, 6794–6799.
(11) Liu, W.; Lin, Q.; Li, H.; Wu, K.; Kobel, I.; Pietryga, J. M.; Klimov, V. I. Mn(2+) Doped Lead Halide Perovskite Nanocrystals with Dual-Color Emission Controlled by Halide Content. J. Am. Chem. Soc. 2016, 138, 14954–14961.
(12) Tang, B.; Ruan, L. J.; Qin, C.; Shu, A.; He, H.; Ma, Y. High Stability and Temperature-Dependent Photoluminescence of Orthorhombic CsPbl3 Nanoparticles. Adv. Opt. Mater. 2020, 8, No. 2000498.
(13) Lu, M.; Zhang, X.; Zhang, Y.; Guo, J.; Shen, X.; Yu, W. W.; Rogach, A. L. Simultaneous Strontium Doping and Chlorine Surface Passivation Improve Luminescence Intensity and Stability of CsPbl3 Nanocrystals Enabling Efficient Light-Emitting Devices. Adv. Mater. 2018, 30, No. 1804691.
(14) Akkerman, Q. A.; Meggiorato, D.; Fang, Z.; De Angelis, F.; Manna, L. Fluorescent Alloy CsPbl-xMnl-xI Nanoparticles with High Structural and Optical Stability. ACS Energy Lett. 2017, 2, 2183–2186.
(15) Masi, S.; Gualdrón-Reyes, A. F.; Mora-Seró, I. Stabilization of Black Perovskite Phase in FAPbI3 and CsPbI3. ACS Energy Lett. 2020, 5, 1974–1985.
(16) Wang, N.; Liu, W.; Zhang, Q. Perovskite-Based Nanocrystals: Synthesis and Applications beyond Solar Cells. Small Methods 2018, 2, No. 1700380.
(17) Swarnkar, A.; Mir, W. J.; Nag, A. Can B-Site Doping or Alloying Improve Thermal- and Phase-Stability of All-Inorganic CsPbl3 (X = Br, I) Perovskites? ACS Energy Lett. 2018, 3, 286–289.
(18) Aleksyan, E.; Aprihaimian, A.; Mukasyan, A. S.; Harutyunyan, V.; Manukyan, K. V. Mechanisms of mechanochemical synthesis of cesium lead halides: pathways toward stabilization of α-CsPbI3. J. Mater. Sci. 2020, 55, 8665–8678.
(19) Zou, Y.; Yuan, Z.; Bie, S.; Gao, F.; Sun, B. Recent progress toward perovskite light-emitting diodes with enhanced spectral and operational stability. Mater. Today Nano 2019, 5, No. 100028.
(20) Xu, L.; Yuan, S.; Zeng, H.; Song, J. A comprehensive review of doping in perovskite nanocrystals/quantum dots: evolution of structure, electronics, optics, and light-emitting diodes. Mater. Today Nano 2019, 6, No. 100036.
(21) Rossi, D.; Parmeck, D.; Dong, Y.; Son, D. H. Dynamics of Exciton–Mn Energy Transfer in Mn-Doped CsPbl3 Perovskite Nanocrystals. J. Phys. Chem. C 2017, 121, 17143–17149.
(22) Bischak, C. G.; Hetherington, C. L.; Wu, H.; Aloni, S.; Ogletry, D. F.; Limmer, D. T.; Ginsberg, N. S. Origin of Reversible Photoinduced Phase Separation in Hybrid Perovskites. Nano Lett. 2017, 17, 1028–1033.
(23) Yao, J. S.; Ge, J.; Wang, K. H.; Zhang, G.; Zhu, B. S.; Chen, C.; Zhang, Q.; Luo, Y.; Yu, S. H.; Yao, H. B. Few-Nanometer-Sized alpha-CsPbl3 Quantum Dots Enabled by Strontium Substitution and Iodide Passivation for Efficient Red-Light Emitting Diodes. J. Am. Chem. Soc. 2019, 141, 2069–2079.
(24) Mir, W. J.; Swarnkar, A.; Nag, A. Postsynthesis Mn-doping in CsPbI$_3$ nanocrystals to stabilize the black perovskite phase. *Nanoscale* 2019, 11, 4278–4286.

(25) Li, J.; Chen, J.; Xu, L.; Liu, S.; Lan, S.; Li, X.; Song, J. A zinc non-halide dopant strategy enables efficient perovskite CsPbI$_3$ quantum dot-based light-emitting diodes. *Mater. Chem. Front.* 2020, 4, 1444–1453.

(26) Zou, S.; Liu, Y.; Li, J.; Liu, C.; Feng, R.; Jiang, F.; Li, Y.; Song, J.; Zeng, H.; Hong, M.; Chen, X. Stabilizing Cesium Lead Halide Perovskite Lattice through Mn(II) Substitution for Air-Stable Light-Emitting Diodes. *J. Am. Chem. Soc.* 2017, 139, 11443–11450.

(27) Mir, W. J.; Jagadeeswararao, M.; Das, S.; Nag, A. Colloidal Mn-Doped Cesium Lead Halide Perovskite Nanoplatelets. *ACS Energy Lett.* 2017, 2, 537–543.

(28) Shen, X.; Zhang, Y.; Kershaw, S. V.; Li, T.; Wang, C.; Zhang, X.; Wang, W.; Li, D.; Wang, Y.; Lu, M.; Zhang, L.; Sun, C.; Zhao, D.; Qin, G.; Bai, X.; Yu, W. W.; Rogach, A. L. Zn-Alloyed CsPbI$_3$ Nanocrystals for Highly Efficient Perovskite Light-Emitting Devices. *Nano Lett.* 2019, 19, 1552–1559.

(29) Shen, W.; Tang, H.; Yang, X.; Cao, Z.; Cheng, T.; Wang, X.; Tan, Z.; You, J.; Deng, Z. Synthesis of highly fluorescent InP/ZnS small-core/thick-shell tetrahedral-shaped quantum dots for blue light-emitting diodes. *J. Mater. Chem. C.* 2017, 5, 8243–8249.

(30) Liu, M.; Jiang, N.; Huang, H.; Lin, J.; Huang, F.; Zheng, Y.; Chen, D. Ni$^{2+}$-doped CsPbI$_3$ perovskite nanocrystals with near-unity photoluminescence quantum yield and superior structure stability for red light-emitting devices. *Chem. Eng. J.* 2021, 413, No. 127547.

(31) Sun, J. K.; Huang, S.; Liu, X. Z.; Xu, Q.; Zhang, Q. H.; Jiang, W. J.; Xue, D. J.; Xu, J. C.; Ma, J. Y.; Ding, J.; Ge, Q. Q.; Gu, L.; Fang, X. H.; Zhong, H. Z.; Hu, J. S.; Wan, L. J. Polar Solvent Induced Lattice Distortion of Cubic CsPbI$_3$ Nanocubes and Hierarchical Self-Assembly into Orthorhombic Single-Crystalline Nanowires. *J. Am. Chem. Soc.* 2018, 140, 11705–11715.

(32) Ruan, L.; Shen, W.; Wang, A.; Zhou, Q.; Zhang, H.; Deng, Z. Stable and conductive lead halide perovskites facilitated by X-type ligands. *Nanoscale* 2017, 9, 7252–7259.

(33) Tang, B.; Ruan, L. J.; Qin, C.; Shu, A.; He, H.; Ma, Y. High Stability and Temperature-Dependent Photoluminescence of Orthorhombic CsPbI$_3$ Perovskite Nanoparticles. *Adv. Opt. Mater.* 2020, 8, No. 2000498.

(34) Yu, J. C.; Kim, D. W.; Kim, D. B.; Jung, E. D.; Park, J. H.; Lee, A.-Y.; Lee, B. R.; Di Nuzzo, D.; Friend, R. H.; Song, M. H. Improving the Stability and Performance of Perovskite Light-Emitting Diodes by Thermal Annealing Treatment. *Adv. Mater.* 2016, 28, 6906–6913.

(35) Li, G.; Wang, H.; Zhu, Z.; Chang, Y.; Zhang, T.; Song, Z.; Jiang, Y. Shape and phase evolution from CsPb$_2$Br$_5$ perovskite nanocubes to tetragonal CsPb$_2$Br$_5$ nanosheets with an indirect bandgap. *Chem. Commun.* 2016, 52, 11296–11299.