Nitrate Ion-Incorporated Stable Perovskite Nanocrystals by a Solvent-Free Mechanochemical Reaction

Gaurav Kumar Nim, Parul Bansal, and Prasenjit Kar*

Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand 247667, India

ABSTRACT: We have synthesized a new class of organolead halide perovskite nanocrystals by a solvent-free mechanochemical green approach. We have developed a new combination of precursors by incorporating nitrate ions into the MAPbBr3 perovskite core. While the presence of nitrate ion is evidenced by Fourier-transform infrared spectra, X-ray diffraction data shows the formation of perovskite nanocrystals. By altering the precursor composition, the morphology of the nanocrystals changes. Photoluminescence properties of these nanocrystals are preserved. Moreover, the stability of these nanocrystals is monitored for a long time, which shows that the incorporation of nitrate ions into the perovskite nanocrystal core does not have any decremental effect on its stability. Nonetheless, this strategy to synthesize perovskite nanocrystals reduces the solvent toxicity.

INTRODUCTION

The organometal halide perovskite materials have attracted considerable attention in recent years due to their high absorption ability and long-range electron-hole diffusion length.1−3 They show potential candidacy for photovoltaic applications and rapidly accomplished stupendous performance.4 This perovskite family obeys ABX3 stoichiometry, where A is the monovalent cation, B is the bivalent metal cation, and X is the halide anion (e.g., Cl−, Br−, I−). These perovskites are highly unstable against moisture;5,6 therefore, protection against moisture is of prime interest. The stability of the perovskite layer can be improved by increasing the intrinsic stability of the perovskites.7−9 While numerous studies on bulk lead halide perovskites exist in the literature, less attention has been directed toward the synthesis and stability of CH3NH3PbX3 quantum dots.9,10 Perovskite nanocrystals display interesting properties such as band-gap expansion, energy level quantization and slower electron−hole fusion.11−15 The potential to tune the optical response of perovskites by altering their size and shape is useful for a range of light-emitting applications.16−18

Numerous methods have been employed to achieve considerable stability of the perovskite materials. Park and co-workers19 investigated the stability of organometallic perovskites using lead nitrate solution as a Pb(NO3)2 source in place of conventional PbI2-dimethylformamide solution. The lead nitrate residue in MAPbI3 slowed the accelerated decomposition as the lead nitrate residue acted as a water scavenger. Miyasaka and co-workers20 have used aqueous lead nitrate solution to synthesize organolead halide perovskites with 12.58% power conversion efficiency and to avoid toxic solvents like dimethylformamide. It was investigated that the formation of MAPbI3 from Pb(NO3)2 is a two-step reaction involving the rapid formation of PbI2 intermediates and the slow reaction of PbI2 and MAI to form MAPbI3. On the other hand, less effort has been devoted on the substitution of a halide counter ion for stability enhancement. Alivisatos and co-workers21 put an effort to stabilize perovskite nanocrystals by encapsulating them into polymer matrices. Similarly, Zhang and co-workers22 have used a technique in which monomer units are polymerized during the synthesis of MAPbBr3 nanocrystals. This perovskite−polymer nanocomposite shows a remarkable stability enhancement in air and resistance to water.

Herein, we have demonstrated highly luminescent nitrate-incorporated new mixed halide perovskite nanocrystals with remarkable stability. We have explored the compositional engineering of a mixed halide for high photoluminescence (PL) properties.

There are only a few reports on substitution of halide ions in perovskite for optoelectronic devices.23−27 To the best of our knowledge, this is the first report that demonstrates the incorporation of a nitrate ion substituting the halide counter-part. We employed a relatively green approach, namely, solvent-free mechanochemical synthetic28 methodology for mixed halide-nitrate-based perovskite nanocrystals.

In this study, nitrate was introduced using the molar ratio of MABr and Pb(NO3)2 to prepare MAPbBr(NO3)2 (PNC-1), while MA(NO3)2 and PbBr2 were used in a molar ratio to synthesize MAPbBr2(NO3) (PNC-2). The tolerance factor
calculated for these compounds (in Supporting Information) does not deviate from that for the perovskite structure. However, we used a different synthetic approach for the solid solution synthesis. Octylamine was used as only capping ligand, while no other stabilizing ligand was used. The absence of oleic acid can keep the solid solution more stable even for several months. The synthesis strategy is depicted in Scheme 1. The detailed synthetic procedure is described in the Supporting Information. The motivation is that the heat generated by mechanical mixing supplies sufficient energy for the crystallization of PNCs. When the precursor solids were ground for 4 min with a rotation speed of 130–140 rpm in a 3 in. diameter mortar, the perovskite crystallization process started; however, the process would be blocked by octylamine. It is worth mentioning that the shape of the nanocrystals is largely controlled by the stoichiometric ratio of nitrate ions. In this report, we have explored (i) the introduction of nitrate ion into the perovskite core, (ii) use of a green synthetic approach, and (iii) octylamine capping ligand as a modified ligand environment. Purification of synthesized perovskite nanocrystals is done using acetone for PNC-2 and ethyl acetate for PNC-1.

RESULT AND DISCUSSION

We have studied the optical properties of these nanocrystals. The green luminescent solid solution of MAPbBr$_3$$_x$(NO$_3$)$_y$ nanocrystals shows absorption and emission peaks at 523 and 555 nm, respectively, as shown in Figure 1a, and at 544 and 553 nm, as shown in Figure 1b for PNC-1 and PNC-2. The absorption edge presents a negligible shift with the change of stoichiometric ratio of the NO$_3$~$^-$ ion, indicating almost similar band gaps of 2.2 and 2.1 eV for PNC-1 and PNC-2, respectively. The small Stokes shifts of 32 nm for PNC-1 and 9 nm for PNC-2 can be attributed to the direct exciton recombination process. Figure S1 (in the Supporting Information) shows the digital image of the mechanochemical synthesis of the perovskite solid solution under daylight and UV light ($\lambda$ = 365 nm). The most striking property of perovskite nanocrystals is their strong photoluminescence. In the PL spectrum, a sharp emission peak for PNC-1 at 555 nm with a full width at half maximum (FWHM) value of 20 and at 553 nm with a FWHM value of 20 nm for PNC-2 can be observed, indicating a color saturation. We have performed experiments for absolute quantum yield with integrated sphere. PLQY for PNC-1 is evaluated as 23% and for PNC-2 as 10%. The existence of nitrate in the perovskite nanocrystals is investigated by Fourier-transform infrared (FT-IR) spectroscopy, and the characteristic peak at 1386 cm$^{-1}$ is observed for nitrate in PNC-1 and PNC-2. Looking into the comparative data of FT-IR spectra, it is observed that the doublet in PNC-1 and PNC-2 in the region 3300–3500 cm$^{-1}$ corresponds to the primary amine group of ligand octylamine. Also, peaks at 2852, 2922, and 2962 cm$^{-1}$ correspond to the $-CH$ stretching of the ligand and peaks at 1600 cm$^{-1}$ correspond to the $C=\equiv C$ mode of the ligand. Finally, 1450 and 1300 cm$^{-1}$ peaks are corresponding to CH bending vibrations. These peaks have shown the presence of ligand on purified perovskite nanocrystals (Figure S2 in the Supporting Information).

To investigate the structural characteristics of the mixed perovskites, we performed X-ray diffraction as shown in Figure 1c. The results show that the X-ray diffraction (XRD) spectra of the two mixed perovskite samples exhibit identical characteristic diffraction. The XRD spectra of mixed perovskite show diffraction peaks at 2$\theta$ = 14.84 and 30.08$^\circ$ corresponding to (001) and (002), for PNC-2. In the case of PNC-1, XRD peaks corresponding to the perovskite structure are at 14.94 and 30.12$^\circ$ for (001) and (002) facets, respectively. XRD details are provided in Tables S1 and S2, in the Supporting Information. In both the perovskites, the peak intensities of (001) and (002) are very high, indicating the stronger preferred orientation of these facets.

A small shift of the diffraction peak of 15.02$^\circ$ is attributed to the nitrate doping (detailed in the Supporting Information Figure S3). It is evident that the high crystallinity and preferred orientation will influence charge dissociation and transport. Notably, XRD is most consistent with the cubic perovskite phase, suggesting that the cubic phase of pure MAPbBr$_3$ is preserved. The XRD data of the precursor is shown in the Supporting Information (Figure S4).

To investigate the surface composition and chemical state of the elements in the sample, XPS spectra of PNC-1 and PNC-2 were recorded. Figure 2a,b shows the survey spectra of PNC-1 and PNC-2, respectively. The survey scan consists of peaks of carbon, nitrogen, bromine, lead, and oxygen ions. The high-resolution spectrum of Pb4f, represented in Figure 2c for PNC-1, shows two lead peaks (doublet) at 139.07 and 143.96 eV. Similarly, Figure 2d shows two lead peaks (doublet) at 138.32 and 143.2 eV for PNC-2. Figure 2e,f shows peaks of the bromine ion, which have some influence of nitrate ions at 68.80, 69.89 and 67.99, 69.01 for PNC-1 and PNC-2, respectively. The N 1s spectrum shown in Figure S5 (in the Supporting Information).
Supporting Information) indicates the existing chemical states of the N element. The peaks at 399.9 eV for PNC-1 and 400.01 eV for PNC-2 originate from methylamine salt. The peaks at 413.7 and 413.2 for PNC-1 and PNC-2, respectively, originate from the incorporated nitrate ion. The O 1s XPS narrow scan as shown in the Supporting Information (Figure S5) for PNC-1 and PNC-2 contains a single peak at 532.41 eV and 532.2, respectively, resulting from oxygen atoms of nitrate (Table S3). XPS narrow scans for C 1s in PNC-1 and PNC-2 are shown in the Supporting Information (Figure S5). The XPS data of all precursors is shown in the Supporting Information (Figure S6).

These newly derived nanocrystals were characterized by transmission electron microscopy (TEM). The TEM image of PNC-1 in Figure 3a,b shows well-defined short rod-shaped nanocrystals. However, the PNC-2 nanocrystals exhibit a long rodlike uniform structure, as represented in Figure 3d,e. The crystalline structure of PNC-1 and PNC-2 can be confirmed by the selected area electron diffraction (SAED) pattern, which gives bright and sharp diffraction spots as shown in Figure 3c,f, respectively. Most of the hybrid perovskites are unstable under electron beam irradiation during high-resolution TEM characterization. The aggregated form of the nanocrystals exhibits cubic nature on a micrometer scale reflected by the SEM image as shown in Figures S7 and S8 (Supporting Information). The presence of all elements in PNC-1 and PNC-2 is further confirmed by energy-dispersive X-ray spectroscopy analysis shown in the Supporting Information (Figures S7 and S8).

Another appealing characteristics of these newly synthesized nanocrystals are their higher sensitivity toward moisture, light irradiation, and heat. In this work, we have tested the stability of PNC-1 and PNC-2 with storage in an ambient environment. PNC-2 shows high stability up to 1410 h (58 days) without degradation (Figure 4a,b). It is worth mentioning that the emission intensity drastically decreased within 24 h and then increased continuously for about 2 months in open air. However, Figure 4c represents the stability of PNC-2 upon addition of water. The stability of PNC-1 is shown in the Supporting Information (Figure S9). Notably, the stability of both the samples increases remarkably with time. PL enhancement might happen because water molecules from...
moisture split into $\text{H}_3\text{O}^+$ and $\text{OH}^-$, which act as active ligands for perovskite nanocrystals.

This active ligand enhances fluorescence, and after some span of time, these water molecules penetrate deep into the structure and degrade it. The other hand, water molecules interact with the nitrate ions. Thus, an increase in nitrate ions decreases the stability of the samples as it is reflected by PNC-1 and PNC-2. However, colloidal solutions of PNC-1 and PNC-2 show reasonable stability in solution, as shown in the Supporting Information (Figure S10). CIE coordinates were calculated as $x = 0.36$ and $y = 0.59$ (for PNC-1) and $x = 0.34$ and $y = 0.62$ (for PNC-2) using CIE 1931 as shown in Figure 4d. The high-quality stable green luminescent PNC-1 and PNC-2 provide opportunities to explore them toward display technology.

Also, time-dependent studies of PNC-2 have been probed through TEM, XRD, XPS, and SEM analyses to know more about its stability (SEM in the Supporting Information, Figure S11). There are no changes in morphology up to 30 days, indicating it to be very stable (Figure 5a). Also, there is no change in XRD of PNC-2 up to 30 days, which is again a strong indication of its stability (Figure 5b). XPS studies reveal about the binding energy of various ions including carbon, nitrogen, oxygen, lead, and bromide ions (Figure 6). Similarly, time-dependent TEM, XRD, SEM, and XPS analyses have been carried out for PNC-1 as shown in Figures S12–S15 in the Supporting Information.

![Figure 4](image1.png) **Figure 4.** (a) Time-dependent intensity vs wavelength emission spectra for PNC-2. (b) Plot of PL intensity vs time for PNC-2. (c) Quenching of emission peak upon addition of water for PNC-2 with respect to time. (d) CIE coordinate plot for PNC-1 and PNC-2.

![Figure 5](image2.png) **Figure 5.** (a) TEM images of PNC-2 with respect to days. (b) Time-dependent XRD pattern of PNC-2.

![Figure 6](image3.png) **Figure 6.** Time-dependent XPS of PNC-2: (a) composition analysis of PNC-2 and (b) high-resolution XPS spectra corresponding to C 1s of PNC-2, (c) N 1s of PNC-2, (d) O 1s of PNC-2, (e) Pb 4f of PNC-2, and (f) Br 3d of PNC-2.

**CONCLUSIONS**

In summary, we have successfully introduced $\text{NO}_3^-$ into the perovskite nanocrystal core using a solvent-free mechanochemical process. This green approach reduces the toxicity caused by the solvent used for the synthesis of these perovskite nanocrystals. Moreover, these newly synthesized nanocrystals exhibit strong luminescent properties. The morphology of the nanocrystals is controlled by changing the ratio of the dopant anion. These nitrate-doped perovskite nanocrystals exhibit better stability in ambient conditions, enabling storage for several months. The detailed study on the stability enhancement of these nitrate-incorporated perovskite nanocrystals in ambient environment is under progress. This work may open up a new avenue for the replication of conventional perovskite nanocrystals with a better stability.

**EXPERIMENTAL SECTION**

All of the chemicals were purchased from commercial sources and were used as received. Lead(II) bromide (99%), methylamine solution (33 wt % in absolute ethanol), and octylamine are purchased from Sigma-Aldrich. Other reagents like lead nitrate, nitric acid (70% in water, SRL), and hydrobromic acid (48 wt % in water, SRL) were ordered from local suppliers.

**Methylammonium Nitrate (MA(NO\textsubscript{3})) Synthesis.** Briefly, in a 50 mL flask, 5.14 mL of CH\textsubscript{3}NH\textsubscript{2}, 40% in methanol, was mixed with 10 mL of ethanol. Then, at room temperature, 6 mL of HNO\textsubscript{3} was added dropwise with continuous stirring. The obtained solution was placed in a rotary evaporator at 60°C for removing all solvents. Then, after washing with diethyl ether several times, the solid product of MANO\textsubscript{3} was obtained.

**Methylammonium Bromide (MABr) Synthesis.** Briefly, in a 50 mL flask, 5.14 mL of CH\textsubscript{3}NH\textsubscript{2}, 40% in methanol, was mixed with 10 mL of ethanol. Then, at room temperature, 6 mL of HBr was added dropwise with continuous stirring. The obtained solution was placed in a rotary evaporator at 60°C for removing all solvents. Then, after washing with diethyl ether several times, the solid product of MABr was obtained.
MAPbBr(NO$_3$)$_2$/MAPbBr$_2$(NO$_3$)$_2$ Mechanochemical Synthesis.

1. For synthesis of MAPbBr(NO$_3$)$_2$, 0.2 mmol of MABr is ground with 0.2 mmol of Pb(NO$_3$)$_2$ in a mortar pestle. Further, 20 μL of octylamine is added and ground continuously for 3–5 min; it gives bright green fluorescence.

2. For synthesis of MAPbBr$_2$(NO$_3$)$_2$, a similar method is followed. First, 0.2 mmol of MA(NO$_3$)$_2$ and 0.2 mmol of PbBr$_2$ are ground in a mortar pestle, and then addition of 20 μL of octylamine with continuous grinding leads to bright green fluorescence.

We have purified the samples with a variety of solvents. Acetone is used for PNC-2, and ethyl acetate is used for PNC-1. After isolating the nanocrystals, we have carried out the product yield for respective perovskite nanocrystals as 70% (PNC-1) and 97% (PNC-2).

For further characterizations including UV and PL measurements, sample preparation had been done be making a thin film on a glass slide with the help of a doctor blade.

**REFERENCES**

(1) Heo, J. H.; Han, H. J.; Lee, M.; Song, M.; Kim, D. H.; Im, S. H. Stable semi-transparent CH$_3$NH$_3$PbI$_3$ planar sandwich solar cells. Energy Environ. Sci. 2015, 8, 2922–2927.

(2) Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaithe, H. J. Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites. Science 2012, 338, 643–647.

(3) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. J. Am. Chem. Soc. 2009, 131, 6050–6051.

(4) Mei, A.; Li, X.; Liu, L.; Ku, Z.; Liu, T.; Rong, Y.; Xu, M.; Hu, M.; Chen, J.; Yang, Y.; Gratzel, M.; Han, H. A hole-conductor-free, fully printable mesoscopic perovskite solar cell with high stability. Science 2014, 345, 295–298.

(5) Niu, G.; Guo, X.; Wang, L. Review of recent progress in chemical stability of perovskite solar cells. J. Mater. Chem. A 2015, 3, 8970–8980.

(6) Agresti, A.; Pescetelli, S.; Cinà, L.; Konios, D.; Kakavelakis, G.; Kymakis, E.; Carlo, A. D. Efficiency and Stability Enhancement in Perovskite Solar Cells by Inserting Lithium-Neutralized Graphene Oxide as Electron Transporting Layer. Adv. Funct. Mater. 2016, 26, 2686–2694.

(7) Noh, J. H.; Im, S. H.; Heo, J. H.; Mandal, T. N.; Seok, S. I. Chemical management for colorful, efficient, and stable inorganic-organic hybrid nanostructured solar cells. Nano Lett. 2013, 13, 1764–1769.

(8) Bansal, P.; Khan, Y.; Nim, G. K.; Kar, P. Surface modulation of solution processed organolead halide perovskite quantum dots to large nanocrystals integrated with silica gel. G. Chem. Commun. 2018, 54, 3508–3511.

(9) Manzi, A.; Tong, Y.; Feucht, J.; Yao, E.-P.; Polavarapu, L.; Urban, A. S.; Feldmann, J. Resonantly enhanced multiple exciton generation through below-band-gap multi-photon absorption in perovskite nanocrystals. Nat. Commun. 2018, 9, No. 1518.

(10) Levchuk, I.; Osvet, A.; Tang, X.; Brandl, M.; Perea, J. D.; Hoegl, F.; Matt, G. J.; Hock, R.; Batentschuk, M.; Brabec, C. J. Correction to Brightly Luminescent and Color-Tunable Formamidinium Lead Halide Perovskite FAPbX$_3$ (X = Cl, Br, I) Colloidal Nanocrystals. Nano Lett. 2017, 17, No. 3993.

(11) Stranks, S. D.; Snaith, H. J. Metal-halide perovskites for photovoltaic and light-emitting devices. Nat. Nanotechnol. 2015, 10, 391–402.

(12) D’Innocenzo, V.; Kandada, A. R. S.; Bastiani, M. D.; Gandini, M.; Petrozza, A. Tuning the Light Emission Properties by Band Gap Engineering in Hybrid Halide Perovskite. J. Am. Chem. Soc. 2014, 136, 17730–17733.

(13) Polavarapu, L.; Nickel, J.; Feldmann, J.; Urban, A. S. Advances in Quantum-Confined Perovskite Nanocrystals for Optoelectronics. Adv. Energy Mater. 2017, 7, No. 1700267.

(14) Sadhanala, A.; Kumar, A.; Pathak, S.; Rao, A.; Steiner, U.; Greenham, N. C.; Snaithe, H. J.; Friend, R. H. Electroluminescence from Organometallic Lead Halide Perovskite-Conjugated Polymer Diodes. Adv. Electron. Mater. 2015, 1, No. 1500008.

(15) Hoye, R. L. Z.; Chua, M. R.; Musselman, K. P.; Li, G.; Lai, M.-L.; Tan, Z.-K.; Greenham, N. C.; MacManus-Driscoll, J. L.; Friend, R. H.; Credgington, D. Enhanced Performance in Fluorene-Free Organometal Halide Perovskite Light-Emitting Diodes using Tunable, Low Electron Affinity Oxide Electron Injectors. Adv. Mater. 2015, 27, 1414–1419.

(16) Protesescu, 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 (CsPbX$_3$ X = Cl, Br and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. Nano Lett. 2015, 15, 3692–3696.

(17) Hintermayr, V. A.; Richter, A. F.; Ehrat, P.; Doblinger, M.; Vanderlinden, W.; Sichert, J. A.; Tong, Y.; Polavarapu, L.; Urban, A. S.; Feldmann, J. Tuning the Optical Properties of Perovskite Nanoplatelets through Composition and Thickness by Ligand-Assisted Excitation. Adv. Mater. 2016, 28, 9478–9485.

(18) Zhang, D.; Eaton, S. W.; Yu, Y.; Dou, L.; Yang, P. Solution-Phase Synthesis of Cesium Lead Halide Perovskite Nanowires. J. Am. Chem. Soc. 2015, 137, 9230–9233.

(19) Shinde, D. V.; Pyeon, L.; Pei, M.; Kim, G.-W.; Yang, H.; Park, T. Enhanced Efficiency and Stability of an Aqueous Lead-Nitrate-Based Organometal Perovskite Solar Cell. ACS Appl. Mater. Interfaces 2017, 9, 14023–14030.

(20) Hsieh, T.-Y.; Wei, T.-C.; Wu, K.-L.; Ikegami, M.; Miyasaka, T. Efficient perovskite solar cells fabricated using an aqueous lead nitrate precursor. Chem. Commun. 2015, 51, 13294–13297.

(21) Raja, S. N.; Bekenstein, Y.; Koc, M. A.; Fischer, S.; Zhang, D.; Lin, L.; Ritchie, R. O.; Yang, P.; Alivisatos, A. P. Encapsulation of
Perovskite Nanocrystals into Macroscale Polymer Matrices: Enhanced Stability and Polarization. ACS Appl. Mater. Interfaces 2016, 8, 35523–35533.

(22) Xin, Y.; Zhao, H.; Zhang, J. Highly Stable and Luminescent Perovskite–Polymer Composites from a Convenient and Universal Strategy. ACS Appl. Mater. Interfaces 2018, 10, 4971–4980.

(23) Shinde, D. V.; Pyeon, L.; Pei, M.; Kim, G.-W.; Yang, H.; Park, T. Enhanced Efficiency and Stability of an Aqueous Lead-Nitrate-Based Organometallic Perovskite Solar Cell. ACS Appl. Mater., Interfaces 2017, 9, 14023–14030.

(24) Abdelmageed, G.; Sully, H. R.; Naghadeh, S. B.; El-Hag Ali, A.; Carter, S. A.; Zhang, J. Z. Improved Stability of Organometal Halide Perovskite Films and Solar Cells toward Humidity via Surface Passivation with Oleic Acid. ACS Appl. Energy Mater. 2018, 1, 387–392.

(25) Huang, H.; Bodnarchuk, M. I.; 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.

(26) Ma, C.; Lo, M.-F.; Lee, C.-S. Stabilization of organometallic halide perovskite nanocrystals in aqueous solutions and their applications in copper ion detection. Chem. Commun. 2018, 54, 5784–5787.

(27) Nagane, S.; Ogale, S. CH3NH3Pb(BF4)3 and (C4H9NH3)2Pb(BF4)2 Family of 3D and 2D Perovskites without and with Iodide and Bromide Ions Substitution. J. Phys. Chem. Lett. 2016, 7, 4757–4762.

(28) Jana, A.; Mittal, M.; Singla, A.; Sapra, S. Solvent-free, mechanochemical syntheses of bulk trihalide perovskites and their nanoparticles. Chem. Commun. 2017, 53, 3046–3049.

(29) Wu, L.; Zhong, Q.; Yang, D.; Chen, M.; Hu, H.; Pan, Q.; Liu, H.; Cao, M.; Xu, Y.; Sun, B.; Zhang, Q. Improving the Stability and Size Tunability of Cesium Lead Halide Perovskite Nanocrystals Using Trioctylphosphine Oxide as the Capping Ligand. Langmuir 2017, 33, 12689–12696.

(30) Gonzalez-Carrero, S. G.; Espallargas, G. M. I.; Galian, R. E.; Prieto, J. P. Blue-luminescent organic lead bromide perovskites: highly disperible and photostable materials. J. Mater. Chem. A 2015, 3, 14039–14045.

(31) Zhang, D.; Yang, Y.; Bekenstein, Y.; Yu, Y.; Gibson, N. A.; Wong, A. B.; Eaton, S. W.; Kornienko, N.; Kong, Q.; Lai, M.; Alivisatos, A. P.; Leone, S. R.; Yang, P. Synthesis of Composition Tunable and Highly Luminescent Cesium Lead Halide Nanowires through Anion-Exchange Reactions. J. Am. Chem. Soc. 2016, 138, 7236–7239.

(32) Zhang, X.; Bai, X.; Wu, H.; Zhang, X.; Sun, C.; Zhang, Y.; Zhang, W.; Zheng, W.; Yu, W. W.; Rogach, A. L. Water-Assisted Size and Shape Control of CsPbBr3 Perovskite Nanocrystals. Angew. Chem., Int. Ed. 2018, 57, 3337–3342.