



Article Suppressed Phase Separation of Mixed-Halide Perovskite Quantum Dots Confined in Mesoporous Metal Organic Frameworks

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Abstract: Mixed-halide perovskite quantum dots (PeQDs) are the most competitive candidates in designing solar cells and light-emitting devices (LEDs) due to their tunable bandgap and high-efficiency quantum yield. However, phase separation in mixed-halide perovskites under illumination can form rich iodine and bromine regions, which change its optical responses. Herein, we synthesize PeQDs combined with mesoporous zinc-based metal organic framework (MOF) crystals, which can greatly improve the stability of anti-anion exchange, including photo-, thermal, and long-term stabilities under illumination. This unique structure provides a solution for improving the performance of perovskite optoelectronic devices and stabilizing mixed-halide perovskite devices.

Keywords: mixed-halide perovskite quantum dots; phase separation; metal organic framework



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1. Introduction

Metal-halide perovskite quantum dots (PeQDs) have become the most competitive semiconductor material in the next generation of photoelectric materials. The characteristics of high quantum yield, wide absorption wavelength, and adjustable band gap make them stand out from traditional materials [1,2]. By changing the halide composition in the quantum dot, the band gap width can be precisely controlled, thus affecting the luminescence properties of the material [3,4]. Although mixed-halide PeQDs have the above-mentioned advantages, their stability is still a limitation for practical applications. Under different conditions, such as humidity [5-8], laser irradiation [9], and temperature [10-12], mixedhalide PeQDs undergo rapid phase separation and degradation, which greatly hinder their practical applications [13–18]. Therefore, solving the stability of mixed-halide PeQDs is the focus of the research at present [19–22]. One feasible strategy to enhance the stability of mixed-halide perovskite nanocrystals (PeNCs) is to design and fabricate hybrid composite materials containing PeQDs [23–26]. Songman Ju et al. prepared mixed-halide CsPbBr₂Cl QDs by introducing alkali metal Rb to suppress the phase separation [27]. By incorporating the chloride into mixed-halide (Br/I) perovskite lattices, McGehee and co-workers boosted the PCE of Si bottom cells to 30% [28]. These works provide solutions for suppressing phase separation and improving the device's performance.

In recent years, a self-assembled mesoporous framework, called metal organic framework (MOFs), which are composited by organic ligands and metal ions through coordination bonds, have been widely used as porous crystal materials with high compatibility [29–31]. The adjustable pore size and high specific surface area of MOFs is a good substrate to grow other materials [32]. These characteristics make MOFs a popular platform for providing a stable environment for other additional materials [33–35]. To date, various quantum dots have been incorporated into MOFs to form a variety of new composite materials with a better performance than intrinsic samples after testing [36]. Although many investigations have been conducted to improve the relative stability by growing PeQDs attached to various host materials, there is still a need to consider stability at a very comprehensive level [37–42]. Therefore, it is necessary to investigate the optical properties of MOF-bound mixed-halide PeQDs [42–45].

In this work, we perform a facile two-step synthesis method for perovskite CsPb(Br_xI_{1-x})₃ QDs embedded in MOF-5 and measure the optical properties of the composites. The various measurements indicate that The CsPb(Br_xI_{1-x})₃ NCs are protected by mesoporous MOF-5 crystals, and the phase separation is suppressed. CsPb(Br_xI_{1-x})₃/MOF-5 composites enhance multiple factors, such as thermal, photo, and long-term stabilities. We can efficiently fix the problem of phase separation and propose a new solution to improve the photoelectric performance of hybrid composites.

2. Materials and Methods

Caesium carbonate (Cs₂CO₃, 99%), lead bromide (PbBr₂, 99%), lead iodide (PbI₂, 99.9%), oleic acid (OA), oleylamine (OLA), 1-Octadecene (ODE, 90%), N,N-Dimethylformamide (DMF, 99.9%), p-Phthalic acid (C₈H₆O₄, 99%), 1,3,5-Trimethylbenzene (C₉H₁₂, 98%), hexadecyl trimethyl ammonium bromide (CTAB, 99%), and n-Hexane (99%) were purchased from Aladdin and used directly without further purification. Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), and trichloromethane (CHCl₃) were purchased from a national pharmaceutical reagent.

2.1. Synthesis of Cs-Oleate Precursor

A total of 0.16 g Cs₂CO₃, 6 mL ODE, and 0.5 mL OA were mixed in a 50 mL 3-necked flask. A magnetic rotor was added to dissolve the Cs₂CO₃, and then heated at 120 °C and 500 rpm under vacuum for 60 min to remove the internal moisture. The mixture was then heated to 150 °C and kept at this temperature for 30 min until the solution became transparent. The synthesized Cs-oleate precursor was collected and kept at room temperature under nitrogen for use.

2.2. Synthesis of CsPbBr_{1.5}I_{1.5} Nanocrystals

In order to synthesize CsPbBr_{1.5}I_{1.5}, NCs 0.0345 g and PbBr₂ 0.042 g PbI₂ were charged in a 50 mL 3-necked flask. A magnetic rotor was added to dissolve the solution efficiently and then degassed at 120 °C under vacuum for 30 min, 500 rpm. A total of 0.5 mL of anhydrous OLA and 0.5 mL of anhydrous OA were, respectively, injected. After the solids of PbBr₂ and PbI₂ were completely dissolved, the mixture's temperature was increased to 150 °C under an N2 atmosphere and 0.45 mL of Cs-oleate solution was rapidly injected. The ice-water bath was immediately used after a 10 s reaction and the solution was cooled to room temperature. The crude solution of CsPbBr_{1.5}I_{1.5} NCs was centrifuged at 8000 rpm for 10 min to remove the supernatant. After the first centrifugation, the particles were dispersed in 1 mL of hexane and centrifuged again at 10,000 rpm for 10 min.

2.3. Synthetic Metal Frame MOF-5

In a typical synthesis, 3.2 mmol zinc nitrate, 1.6 mmol terephthalic acid, and 40 mL DMF were loaded with a magnetic rotor into the reactor's inner cylinder. A total of 0.96 mmol CTAB and 1.92 mmol TMB were added, respectively, to the solution during the stirring. After all the solid powder was dissolved, the magnetic rotor was removed and the reaction kettle was placed in a high-temperature drying box at 135 °C for 24 h. In order to remove the remaining raw materials, DMF was used to filtrate the reaction product 5 times. Then, it was washed with chloroform 2–3 times to remove the DMF. Then, the pure reactants were dried in a vacuum oven at 80 °C for 8 h, and the obtained MOF-5 was collected for final use.

2.4. Synthesis of CsPbBr_{1.5}I_{1.5}@MOF-5 Composites [35]

The CsPbBr_{1.5}I_{1.5}@MOF-5 composites were synthesized by mixing the previous product. Typically, 0.5 mL CsPbBr_{1.5}I_{1.5} and 30 mg of activated MOF-5 powder were charged into a test tube. Then, the solution was stirred by a magnetic rotor for 10 min. The product was obtained by filtration and washed with n-hexane 5 times to remove the NCs on the surface. Finally, a vacuum-drying oven was used to dehydrate the sample at 40 °C for 30 min.

2.5. Optical Characterizations

The CsPbBr_{1.5}I_{1.5} NC and CsPbBr_{1.5}I_{1.5}/MOF-5 samples could be used directly after synthesis or stored for several months in a glove box filled with Ar gas, whether fresh or stored samples present very similar phase-segregation properties. For the later measurement of ensemble- or single-particle optical characterizations at room temperature, one drop of the concentrated or diluted solution of colloidal NCs (CsPbBr_{1.5}I_{1.5}) was spin-coated with 4000RPM for 1 min onto a fused silica substrate to form a solid film. A picosecond diode laser working at a 5 MHz repetition rate provided a 405 nm output, and the laser penetrated an immersion-oil objective (numerical aperture, 1.4) and finally focused on the sample substrate. The PL signal of the ensemble NCs was collected by the same objective and sent through a 0.5 m spectrometer to a charge-coupled-device camera for the PL spectral measurement with an integration time of 1 s.

3. Results and Discussion

A two-step method was introduced to prepare the CsPbBr_{1.5} $I_{1.5}$ /MOF-5 composites, including the growth processes of the pore structure of MOF-5 and CsPbBr_{1.5}I_{1.5} NCs synthesis processes; this is shown in Figure 1a, schematically. Owing to its ordered, abundant, and uniform mesoporous structure, mesoporous MOF-5 was chosen as an encapsulation matrix, which provided an excellent space for the restrictive growth of PeQDs. First, we prepared the pore structure of MOF-5 crystals, and templating agents cetyltrimethylammonium bromide and 1,3,5-trimethylbenzene were used to expand the mesoporous product (135 °C, 24 h). Additionally, we mixed the CsPbBr_{1.5}I_{1.5} QDs with the mesoporous MOF-5 crystals, physically, in solution to obtain the CsPbBr_{1.5} $I_{1.5}$ /MOF-5 composites. Finally, we used a vacuum-drying oven for 30 min at 40 °C to dry the powders to obtain the CsPbBr_{1.5} $I_{1.5}$ /MOF-5 composite. We found that the micro-holes of the mesoporous metal organic framework (MOF-5) could govern the size of CsPbBr_{1.5}I_{1.5} QDs as a matrix. Photos of the MOF-5 powder under and without UV light are presented in Figure 1b. The MOF-5 composites immediately turned red with the injection of the CsPbBr_{1.5}I_{1.5} solution and became orange under UV light. The emission of CsPbBr_{1.5} $I_{1.5}$ @MOF-5 powder was bright orange with a 365 nm illumination, and optical fluorescence pictures are also presented in Figure 1b.

In order to demonstrate the microstructure properties, we measured the SEM of the MOF-5 and CsPbBr_{1.5}I_{1.5}/MOF-5 composites, and the images are shown in Figure 2a,b, respectively. From the SEM images, it can be observed that MOF-5 has a 10 μ m edge-lengthened cubic microcrystal morphology with a 0.5 μ m aperture (Figure S1a), and CsPbBr_{1.5}I_{1.5} QDs can be perfectly embraced in the MOF-5 matrix structure, and the sizes of CsPbBr_{1.5}I_{1.5} QDs range from 10 to 20 nm. Additionally, Figure 2c shows an amplified illustration of a high-resolution TEM image of the CsPbBr_{1.5}I_{1.5}/MOF-5 composite. Figure S1b shows the CsPbBr_{1.5}I_{1.5} cubic phase of the (110) plane corresponding to clear lattice fringe spacing, which is 0.41 nm. The particle size statistics of CsPbBr_{1.5}I_{1.5}, MOF-5, and CsPbBr_{1.5}I_{1.5}/MOF-5 are shown in Figure S2 and fitted by the Gaussian function. Figure 2d–g shows the EDS mapping of this hybrid material with a uniform distribution of elements Cs, Pb, I, and Br; this reflects the perfect encapsulation of the perovskite nanocrystal into the MOF-5 structure. Elemental specific gravity is consistent with that described in the previous study [27,46], and corresponds to the chemical composition of the material. Therefore, CsPbBr_{1.5}I_{1.5} QDs are uniformly distributed in the pores of MOF-5, which are

successfully encapsulated in the framework of the MOF-5 matrix. The TEM images provide clear evidence that the MOF-5 matrix protects the mixed-halide perovskite QDs, and that it improves the stability of CsPbBr_{1.5}I_{1.5} QDs.



Figure 1. (a) Schematic illustration of the formation process of CsPbBr_{1.5}I_{1.5}@MOF-5 composites. (b) Illustrative images of the MOF-5 precursor and CsPbBr_{1.5}I_{1.5}@MOF-5 composite in daylight and under 405 nm UV light and its fluorescence morphology.



Figure 2. (a) SEM image of MOF-5, (b) SEM image of CsPbBr_{1.5}I_{1.5}/MOF-5, corresponding HR-TEM images (c) are shown as insets, and (**d**–**g**) EDS elemental mapping images of CsPbBr_{1.5}I_{1.5}/MOF-5.

In order to investigate the phase composition of CsPbBr_{1.5}I_{1.5}/MOF-5 composites, we used powder XRD to analyze the samples. The MOF-5 sample showed good crystallinity with sharp XRD peaks, and it was highly consistent with the standard card of MOF-5. The

yellow line in the figure represents the characteristic peaks of MOF-5, which all correspond well with the measurements. Meanwhile, the XRD peaks of $CsPbBr_{1.5}I_{1.5}$ QDs can also be observed. Compared with the standard XRD card of CsPbBr₃, all diffraction peaks of CsPbBr_{1.5}I_{1.5} QDs shifted to small angles. The XRD pattern of the CsPbBr_{1.5}I_{1.5}/MOF-5 composite presents no significant CsPbBr_{1.5}I_{1.5} peaks (Figure 3a). Figure 3b shows the normalized PL and optical absorption spectra of the CsPbBr_{1.5}I_{1.5} and CsPbBr_{1.5}I_{1.5}/MOF-5 QDs. Both samples were excited by a 405 nm pulsed laser and emitted light at about 610 nm. The PL emission spectra of CsPbBr_{1.5}I_{1.5} and CsPbBr_{1.5}I_{1.5}/MOF-5 QDs were stokes-shifted with respect to the optical absorption spectra. Compared with the emission peak position and absorption spectra of these two samples, only a few differences are shown in Figure 3b. Therefore, the MOF-5 matrix slightly improved the luminescence of $CsPbBr_{1.5}I_{1.5}$ QDs and retained the same optical properties. Figure S3 shows the emissions of pure MOF-5. Under excitation at 355 nm, a band-edge emission of MOF-5 appeared at about 450 nm and showed a wide FWHM of around 110 nm. The UV-Vis absorption spectrum of MOF-5 showed that there was an absorption stage at about 370 nm and its absorption edge was about 325 nm. For the 405 nm laser used in subsequent experiments, MOF-5 could hardly absorb effectively; therefore, the influence of MOF-5 on the spectrum could be ignored when testing the composites.



Figure 3. (a) X-ray diffraction patterns of the MOF-5, CsPbBr_{1.5}I_{1.5}, and CsPbBr_{1.5}I_{1.5}/MOF-5; (b) absorption and PL spectra of CsPbBr_{1.5}I_{1.5} QDs with and without MOF-5; (c) time-resolved PL lifetimes of CsPbBr_{1.5}I_{1.5} and CsPbBr_{1.5}I_{1.5}/MOF-5.

PL lifetimes were measured to further investigate the carrier dynamics of CsPbBr_{1.5}I_{1.5}/MOF-5 QDs. The time-resolved PL decay values of CsPbBr_{1.5}I_{1.5} and CsPbBr_{1.5}I_{1.5}/MOF-5 QDs are shown in Figure 3c. For CsPbBr_{1.5}I_{1.5} QDs, the average PL lifetime was 6.5 ns and it increased to 11.9 ns for CsPbBr_{1.5}I_{1.5}/MOF-5. It can be found that the lifetime of pristine CsPbBr_{1.5}I_{1.5} QDs is shorter than CsPbBr_{1.5}I_{1.5} QDs/MOF-5. Obviously, these treatments enhance the PL lifetime of CsPbBr_{1.5}I_{1.5} QDs and change the luminescence process. Through the protection of the mesoporous MOF-5 matrix, the non-radiative recombination pathway, such as the Auger recombination of CsPbBr_{1.5}I_{1.5} QDs, was efficiently restricted, and this result consists with the high PL quantum yield of CsPbBr_{1.5}I_{1.5}/MOF-5 composites.

In order to investigate the PL emission stability and effect of continuous laser illumination of CsPbBr_{1.5}I_{1.5} QDs, we used a constant-intensity laser that could provide an excitation density of 358 mW/cm² to investigate its PL spectra. The detailed schematic diagram of the experimental process is shown in Figure S4a. With increasing the laser excitation time, an obvious continuous blue-shift of about ~360 meV was observed in the emission peak and shifted from 2 to 2.36 eV. The PL intensity of the lower-energy peak at 610 nm decreased and the peak at 510 nm was insistently increased, which signified a phase separation. Then, we investigated the blue-shift induced by photoexcitation in PL spectra; excitation power-density-dependent PL measurements were also performed, as shown in Figure 4a,d. Figure 4a,b clearly shows both peak's PL intensities tend to saturate after around 5 min of illumination, and both peaks show comparable PL intensities in the

spectrum. At a lower excitation density (1 mW/cm²), the blue-shift process was obviously slower and the PL intensity increased over exposure time and finally reach the maximum value. The blue-shift and PL intensities increased at higher excitation power densities with the exposure time. The stronger the excitation power, the quicker the sample gained a blue shift. It was indicated that the formation of low-energy sub-bandgap states and the filling of existing trap sites at higher excitation power densities caused this phenomenon. In particular, the standard PL emission from CsPbBr₃ perovskite NCs was detected when the mixed-halide perovskite NPs blue-shifted to around 2.36 eV by photoexcitation. This may have been due to the migration of halide ions and the formation of an iodide-rich perovskite phase; thus, the bromine-rich domain's luminescence dominated its PL emission.



Figure 4. Time-dependent PL spectra of CsPbBr_{1.5}I_{1.5} (**a**) before and (**b**) after 5 min laser irradiation at different excitation power densities; time-dependent PL spectra of CsPbBr_{1.5}I_{1.5}/MOF-5 (**c**) before and (**d**) after 5 min laser irradiation at different excitation power densities.

However, CsPbBr_{1.5}I_{1.5} NCs, which are embedded in the MOF matrix, showed different characteristics between the uncovered samples; Figure 4c,d presents the highly suppressed phase segregation though MOF treatment. Under a continuous excitation

intensity ($\leq 1 \text{ mW/cm}^2$), it only red-shifted at around 50 nm with a single iodide-rich phase. Moreover, it maintained a constant PL intensity at 1.9 eV and the CsPbBr_{1.5}I_{1.5}/MOF-5 remained stable with no further phase segregation occurring under a period of intense irradiation because the MOF framework limited anion transfer. After a high excitation power P_{exc} = 5 mW/cm² of 5 min of illumination, the PL peak showed only ~55 nm shifts and a slow red shift.

The thermal stabilities of CsPbBr_{1.5}I_{1.5}/MOF-5 composites and CsPbBr_{1.5}I_{1.5} were also investigated. A detailed schematic diagram of the experimental process is shown in Figure S4b. The PL at different temperatures through placing the samples on the heating platform was measured. Considering the material showed a greater degree of phase separation under low-intensity illumination, and in order to analyze the influence of heat, we used a pulsed-laser light (405 nm, 440 mW/cm²) with a lower power density to investigate this process.

As the temperature increased, the PL intensities of both materials decreased. Inevitably, a high temperature caused the degradation of CsPbBr_{1.5}I_{1.5} QDs to a certain extent. We observed the phenomenon of both samples under three different temperatures and investigated the thermal stability. Figure 5a,b show the variation in untreated samples under different temperature surroundings; it divides two peaks that correspond to phase separation. At 25 °C, the PL spectrum shows a weak difference between the two samples; however, when the temperature reaches 60 °C, CsPbBr_{1.5}I_{1.5} QDs presents phase separation in the short term and the PL intensity decreases to 69% of its initial intensity. The PL intensity becomes weaker when the temperature increases to 100 $^{\circ}$ C, and the phase separates rapidly into the bromine-rich zone. Figure 5c,d show the change in the PL spectra of CsPbBr_{1.5}I_{1.5}/MOF-5 with the increase in temperature. At 25 °C, CsPbBr_{1.5}I_{1.5}/MOF-5 presents excellent stability and almost no phase separation. By increasing the temperature to 60 °C, the spectrum only shows a bulge at 510 nm, which confirmed the formation of only a small fraction of bromine-rich regions. Even at 100 °C, the phase separation was still not obvious. Compared with the pristine sample, $CsPbBr_{1.5}I_{1.5}/MOF-5$ only had one peak that shows extreme stability under high temperatures where no phase separation appears. This reflects that the MOF-5 matrix can effectively enhance the thermal stability of QDs and inhibit phase separation.



Figure 5. Cont.



Figure 5. PL spectra of CsPbBr_{1.5}I_{1.5} (**a**) before and (**b**) after 3 min of laser irradiation at same laser powers. PL spectra of CsPbBr_{1.5}I_{1.5}/MOF-5 (**c**) before and (**d**) after 3 min of laser irradiation at same laser powers.

In addition, we measured the temporal stability of the samples with respect to phase separation and compared the decay of the PeQDs of wrapped and unwrapped MOF-5 samples. Figure S5 shows the PL changes in $CsPbBr_{1.5}I_{1.5}$ and $CsPbBr_{1.5}I_{1.5}/MOF-5$ within 30 days. It can be observed that $CsPbBr_{1.5}/MOF-5$ only shows about a 10% PL attenuation, while CsPbBr_{1.5}I_{1.5}suffers more severe PL quenching due to the lack of protection of MOF-5. Then, the recovery of the samples after phase separation was studied. After laser irradiation at 20 µW for 5 min, the laser irradiation was stopped and the PL measurements were performed on CsPbBr_{1.5}I_{1.5}/MOF-5 composites after an interval of 20 min. Figure S6a presents the phase separation of PeQDs without MOF-5, and Figure S6b shows how PeQDs are protected by MOF-5. It can be seen that, for the samples without the protection of MOF-5, a small degree of recovery occurred after 20 min. For the samples protected by MOF-5, there was no significant change after 20 min. The same test was then used to characterize the temperature effect of CsPbBr_{1.5}I_{1.5}/MOF-5 composites. For a sample heated at 100 °C for 3 min, Figure S6c shows the spectra of PeQDs without MOF-5 protection after 20 min of returning to room temperature. Figure S6d presents the spectrum of CsPbBr_{1.5} $I_{1.5}$ /MOF-5 composites after 20 min. It can be seen that MOF-5 has a very obvious inhibitory effect on ion migration, whether this occurred in the recovery or phase-separation process.

4. Conclusions

In conclusion, we introduced an efficient method that can embed CsPbBr_{1.5}I_{1.5} QDs into a mesoporous MOF-5 matrix to delicately synthesize CsPbBr_{1.5}I_{1.5}/MOF-5 composites under ambient conditions. The mesoporous MOF-5 crystals protect the CsPbBr_{1.5}I_{1.5} QDs from making contact with the other adjacent PeQDs and embed CsPbBr_{1.5}I_{1.5} QDs to produce a good matrix. By comparing the stability of CsPbBr_{1.5}I_{1.5} and CsPbBr_{1.5}I_{1.5}/MOF-5 composites, we concluded that phase separation was well suppressed by mesoporous MOF-5 for mixed-halide PeQDs. The stability properties (long-term, photo-, and thermal stabilities, and the behavior against anion exchange) of CsPbBr_{1.5}I_{1.5}/MOF-5 composites could be maintained while improving the excellent PL properties. Thus, introducing PeQDs into MOF-5 crystals with mesoporous structures can help to develop efficient optoelectronic devices and solar cells, as well as determined the principle of phase separation in mixed-halide PeQDs.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano13101655/s1.

Author Contributions: X.T., Q.X. and C.Y. conceived and planned the project. H.D. and D.M. performed and analyzed the spectroscopy experiments. Q.C., Y.X. and D.M. synthesized the materials. Q.X. wrote the paper and discussed this with the other authors. All authors have read and agreed to the published version of the manuscript.

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References

- Beal, R.E.; Slotcavage, D.J.; Leijtens, T.; Bowring, A.R.; Belisle, R.A.; Nguyen, W.H.; Burkhard, G.F.; Hoke, E.T.; McGehee, M.D. Cesium Lead Halide Perovskites with Improved Stability for Tandem Solar Cells. J. Phys. Chem. Lett. 2016, 7, 746–751. [CrossRef] [PubMed]
- McMeekin, D.P.; Sadoughi, G.; Rehman, W.; Eperon, G.E.; Saliba, M.; Hörantner, M.T.; Haghighirad, A.; Sakai, N.; Korte, L.; Rech, B.; et al. A mixed-cation lead mixed-halide perovskite absorber for tandem solar cells. *Science* 2016, 351, 151–155. [CrossRef] [PubMed]
- Sutter-Fella, C.M.; Li, Y.; Amani, M.; Ager, J.W.I.; Toma, F.M.; Yablonovitch, E.; Sharp, I.D.; Javey, A. High Photoluminescence Quantum Yield in Band Gap Tunable Bromide Containing Mixed Halide Perovskites. *Nano Lett.* 2016, 16, 800–806. [CrossRef] [PubMed]
- 4. 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. [CrossRef]
- Brivio, F.; Caetano, C.; Walsh, A. Thermodynamic Origin of Photoinstability in the CH₃NH₃Pb(I_{1-x}Br_x)₃ Hybrid Halide Perovskite Alloy. *J. Phys. Chem. Lett.* 2016, 7, 1083–1087. [CrossRef]
- 6. Hoke, E.T.; Slotcavage, D.J.; Dohner, E.R.; Bowring, A.R.; Karunadasa, H.I.; McGehee, M.D. Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics. *Chem. Sci.* **2015**, *6*, 613–617. [CrossRef]
- Yang, X.; Yan, X.; Wang, W.; Zhu, X.; Li, H.; Ma, W.; Sheng, C. Light induced metastable modification of optical properties in CH₃NH₃PbI_{3-x}Br_x perovskite films: Two-step mechanism. Org. Electron. 2016, 34, 79–83. [CrossRef]
- 8. Yoon, S.J.; Draguta, S.; Manser, J.S.; Sharia, O.; Schneider, W.F.; Kuno, M.; Kamat, P.V. Tracking Iodide and Bromide Ion Segregation in Mixed Halide Lead Perovskites during Photoirradiation. *ACS Energy Lett.* **2016**, *1*, 290–296. [CrossRef]
- Sadhanala, A.; Deschler, F.; Thomas, T.H.; Dutton, S.E.; Goedel, K.C.; Hanusch, F.C.; Lai, M.L.; Steiner, U.; Bein, T.; Docampo, P.; et al. Preparation of Single-Phase Films of CH₃NH₃Pb(I_{1-x}Br_x)₃ with Sharp Optical Band Edges. *J. Phys. Chem. Lett.* 2014, *5*, 2501–2505. [CrossRef]
- 10. Ruess, R.; Benfer, F.; Böcher, F.; Stumpp, M.; Schlettwein, D. Stabilization of Organic–Inorganic Perovskite Layers by Partial Substitution of Iodide by Bromide in Methylammonium Lead Iodide. *ChemPhysChem* **2016**, *17*, 1505–1511. [CrossRef]
- 11. Bischak, C.G.; Hetherington, C.L.; Wu, H.; Aloni, S.; Ogletree, D.F.; Limmer, D.T.; Ginsberg, N.S. Origin of Reversible Photoinduced Phase Separation in Hybrid Perovskites. *Nano Lett.* **2017**, *17*, 1028–1033. [CrossRef] [PubMed]
- 12. Slotcavage, D.J.; Karunadasa, H.I.; McGehee, M.D. Light-Induced Phase Segregation in Halide-Perovskite Absorbers. *ACS Energy Lett.* **2016**, *1*, 1199–1205. [CrossRef]
- Pan, J.; Shang, Y.; Yin, J.; De Bastiani, M.; Peng, W.; Dursun, I.; Sinatra, L.; El-Zohry, A.M.; Hedhili, M.N.; Emwas, A.-H. Bidentate ligand-passivated CsPbI₃ perovskite nanocrystals for stable near-unity photoluminescence quantum yield and efficient red light-emitting diodes. *J. Am. Chem. Soc.* 2017, 140, 562–565. [CrossRef]
- 14. Huang, H.; Chen, B.; Wang, Z.; Hung, T.F.; Susha, A.S.; Zhong, H.; Rogach, A.L. Water resistant CsPbX₃ nanocrystals coated with polyhedral oligomeric silsesquioxane and their use as solid state luminophores in all-perovskite white light-emitting devices. *Chem. Sci.* **2016**, *7*, 5699–5703. [CrossRef]
- 15. Li, Z.-J.; Hofman, E.; Li, J.; Davis, A.H.; Tung, C.-H.; Wu, L.-Z.; Zheng, W. Photoelectrochemically Active and Environmentally Stable CsPbBr₃/TiO₂ Core/Shell Nanocrystals. *Adv. Funct. Mater.* **2018**, *28*, 1704288.
- 16. Lu, C.; Li, H.; Kolodziejski, K.; Dun, C.; Huang, W.; Carroll, D.; Geyer, S.M. Enhanced stabilization of inorganic cesium lead triiodide (CsPbI₃) perovskite quantum dots with tri-octylphosphine. *Nano Res.* **2018**, *11*, 762–768. [CrossRef]
- Qian, C.-X.; Deng, Z.-Y.; Yang, K.; Feng, J.; Wang, M.-Z.; Yang, Z.; Liu, S.; Feng, H.-J. Interface engineering of CsPbBr₃/TiO₂ heterostructure with enhanced optoelectronic properties for all-inorganic perovskite solar cells. *Appl. Phys. Lett.* 2018, 112, 093901. [CrossRef]

- 18. Li, Z.; Kong, L.; Huang, S.; Li, L. Highly luminescent and ultrastable CsPbBr₃ perovskite quantum dots incorporated into a silica/alumina monolith. *Angew. Chem.* **2017**, *129*, 8246–8250.
- Dirin, D.N.; Protesescu, L.; Trummer, D.; Kochetygov, I.V.; Yakunin, S.; Krumeich, F.; Stadie, N.P.; Kovalenko, M.V. Harnessing defect-tolerance at the nanoscale: Highly luminescent lead halide perovskite nanocrystals in mesoporous silica matrixes. *Nano Lett.* 2016, 16, 5866–5874. [CrossRef] [PubMed]
- Sun, J.-Y.; Rabouw, F.T.; Yang, X.-F.; Huang, X.-Y.; Jing, X.-P.; Ye, S.; Zhang, Q.-Y. Facile two-step synthesis of all-inorganic perovskite CsPbX₃ (X = Cl, Br, I) zeolite-Y composite phosphors for potential backlight display application. *Adv. Funct. Mater.* 2017, 27, 1704371. [CrossRef]
- 21. Zhang, X.; Lv, L.; Ji, L.; Guo, G.; Liu, L.; Han, D.; Wang, B.; Tu, Y.; Hu, J.; Yang, D. Self-assembly of one-dimensional nanocrystal superlattice chains mediated by molecular clusters. *J. Am. Chem. Soc.* **2016**, *138*, 3290–3293. [CrossRef]
- 22. Yang, Z.; Rajagopal, A.; Jo, S.B.; Chueh, C.-C.; Williams, S.; Huang, C.-C.; Katahara, J.K.; Hillhouse, H.W.; Jen, A.K.-Y. Stabilized wide bandgap perovskite solar cells by tin substitution. *Nano Lett.* **2016**, *16*, 7739–7747. [CrossRef] [PubMed]
- 23. Hu, M.; Bi, C.; Yuan, Y.; Bai, Y.; Huang, J. Stabilized wide bandgap MAPbBr_xI_{3-x} perovskite by enhanced grain size and improved crystallinity. *Adv. Sci.* **2016**, *3*, 1500301. [CrossRef]
- Abdi-Jalebi, M.; Andaji-Garmaroudi, Z.; Cacovich, S.; Stavrakas, C.; Philippe, B.; Richter, J.M.; Alsari, M.; Booker, E.P.; Hutter, E.M.; Pearson, A.J. Maximizing and stabilizing luminescence from halide perovskites with potassium passivation. *Nature* 2018, 555, 497–501. [CrossRef]
- Brennan, M.C.; Draguta, S.; Kamat, P.V.; Kuno, M. Light-induced anion phase segregation in mixed halide perovskites. ACS Energy Lett. 2017, 3, 204–213.
- Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O.M. Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. *Science* 2002, 295, 469–472. [CrossRef] [PubMed]
- Ju, S.; Mao, C.; Liu, Y.; Zhu, Y.; Xu, Z.; Yang, K.; Guo, T.; Hu, H.; Li, F. Inhibiting phase separation of perovskite quantum dots for achieving stable blue light-emitting diodes. Org. Electron. 2023, 113, 106718. [CrossRef]
- Xu, J.; Boyd, C.C.; Yu, Z.J.; Palmstrom, A.F.; Witter, D.J.; Larson, B.W.; France, R.M.; Werner, J.; Harvey, S.P.; Wolf, E.J.; et al. Triple-halide wide–band gap perovskites with suppressed phase segregation for efficient tandems. *Science* 2020, 367, 1097–1104. [CrossRef]
- 29. Cao, S.; Gody, G.; Zhao, W.; Perrier, S.; Peng, X.; Ducati, C.; Zhao, D.; Cheetham, A.K. Hierarchical bicontinuous porosity in metal–organic frameworks templated from functional block co-oligomer micelles. *Chem. Sci.* 2013, *4*, 3573–3577. [CrossRef]
- Shen, K.; Zhang, L.; Chen, X.; Liu, L.; Zhang, D.; Han, Y.; Chen, J.; Long, J.; Luque, R.; Li, Y. Ordered macro-microporous metal-organic framework single crystals. *Science* 2018, 359, 206–210. [CrossRef] [PubMed]
- 31. Qiu, L.-G.; Xu, T.; Li, Z.-Q.; Wang, W.; Wu, Y.; Jiang, X.; Tian, X.-Y.; Zhang, L.-D. Hierarchically micro-and mesoporous metal–organic frameworks with tunable porosity. *Angew. Chem. Int. Ed.* **2008**, *47*, 9487–9491. [CrossRef]
- Lee, K.J.; Lee, J.H.; Jeoung, S.; Moon, H.R. Transformation of metal–organic frameworks/coordination polymers into functional nanostructured materials: Experimental approaches based on mechanistic insights. *Acc. Chem. Res.* 2017, 50, 2684–2692. [CrossRef]
- Zhang, C.; Wang, B.; Li, W.; Huang, S.; Kong, L.; Li, Z.; Li, L. Conversion of invisible metal-organic frameworks to luminescent perovskite nanocrystals for confidential information encryption and decryption. *Nat. Commun.* 2017, *8*, 1138. [CrossRef]
- 34. Chen, Z.; Gu, Z.-G.; Fu, W.-Q.; Wang, F.; Zhang, J. A confined fabrication of perovskite quantum dots in oriented MOF thin film. *ACS Appl. Mater. Interfaces* **2016**, *8*, 28737–28742. [CrossRef]
- 35. Zhang, D.; Xu, Y.; Liu, Q.; Xia, Z. Encapsulation of CH₃NH₃PbBr₃ perovskite quantum dots in MOF-5 microcrystals as a stable platform for temperature and aqueous heavy metal ion detection. *Inorg. Chem.* **2018**, *57*, 4613–4619. [CrossRef]
- Jin, S.; Son, H.-J.; Farha, O.K.; Wiederrecht, G.P.; Hupp, J.T. Energy transfer from quantum dots to metal–organic frameworks for enhanced light harvesting. J. Am. Chem. Soc. 2013, 135, 955–958. [CrossRef]
- Aguilera-Sigalat, J.; Bradshaw, D. Synthesis and applications of metal-organic framework–quantum dot (QD@ MOF) composites. Coord. Chem. Rev. 2016, 307, 267–291. [CrossRef]
- Nickerl, G.; Senkovska, I.; Kaskel, S. Tetrazine functionalized zirconium MOF as an optical sensor for oxidizing gases. *Chem. Commun.* 2015, 51, 2280–2282. [CrossRef]
- 39. Wang, P.; Zhao, J.; Li, X.; Yang, Y.; Yang, Q.; Li, C. Assembly of ZIF nanostructures around free Pt nanoparticles: Efficient size-selective catalysts for hydrogenation of alkenes under mild conditions. *Chem. Commun.* **2013**, *49*, 3330–3332. [CrossRef]
- Ren, J.; Li, T.; Zhou, X.; Dong, X.; Shorokhov, A.V.; Semenov, M.B.; Krevchik, V.D.; Wang, Y. Encapsulating all-inorganic perovskite quantum dots into mesoporous metal organic frameworks with significantly enhanced stability for optoelectronic applications. *Chem. Eng. J.* 2019, 358, 30–39. [CrossRef]
- 41. Zhang, D.; Zhou, W.; Liu, Q.; Xia, Z. CH₃NH₃PbBr₃ perovskite nanocrystals encapsulated in lanthanide metal–organic frameworks as a photoluminescence converter for anti-counterfeiting. *ACS Appl. Mater. Interfaces* **2018**, *10*, 27875–27884. [CrossRef]
- 42. Ren, J.; Zhou, X.; Wang, Y. Dual-emitting CsPbX₃@ ZJU-28 (X = Cl, Br, I) composites with enhanced stability and unique optical properties for multifunctional applications. *Chem. Eng. J.* **2020**, *391*, 123622. [CrossRef]

- 43. Kong, Z.-C.; Liao, J.-F.; Dong, Y.-J.; Xu, Y.-F.; Chen, H.-Y.; Kuang, D.-B.; Su, C.-Y. Core@ shell CsPbBr₃@ zeolitic imidazolate framework nanocomposite for efficient photocatalytic CO₂ reduction. *ACS Energy Lett.* **2018**, *3*, 2656–2662. [CrossRef]
- 44. Mei, S.; Yang, B.; Wei, X.; Dai, H.; Chen, Z.; Cui, Z.; Zhang, G.; Xie, F.; Zhang, W.; Guo, R. Facile synthesis and optical properties of CsPbX₃/ZIF-8 composites for wide-color-gamut display. *Nanomaterials* **2019**, *9*, 832. [CrossRef]
- Cha, J.-H.; Noh, K.; Yin, W.; Lee, Y.; Park, Y.; Ahn, T.K.; Mayoral, A.; Kim, J.; Jung, D.-Y.; Terasaki, O. Formation and encapsulation of all-inorganic lead halide perovskites at room temperature in metal–organic frameworks. *J. Phys. Chem. Lett.* 2019, 10, 2270–2277. [CrossRef]
- 46. Karimzadeh, Z.; Javanbakht, S.; Namazi, H. Carboxymethylcellulose/MOF-5/Graphene oxide bio-nanocomposite as antibacterial drug nanocarrier agent. *Bioimpacts* 2018, *9*, 5–13. [CrossRef]

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