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ABSTRACT: Metal-halide perovskite materials are highly attractive materials for optoelectronic applications. However, the instability of perovskite materials caused by moisture and heat-induced degradation impairs future prospects of using these materials. Here we employ water to directly transform films of the three-dimensional (3D) perovskite CsPbBr₃ to stable two-dimensional (2D) perovskite-related CsPb₂Br₅. A sequential dissolution-recrystallization process governs this water induced transformation under PbBr₂ rich condition. We find that these post-synthesized 2D perovskite-related material films exhibit excellent stability against humidity and high photoluminescence quantum yield. We believe that our results provide a new synthetic method to generate stable 2D perovskite-related materials that could be applicable for light emitting device applications.

Introduction

Organic-inorganic hybrid perovskites are attractive semiconducting materials because of their extraordinary electrical and optical properties that have been studied intensively in the field of photovoltaics,¹⁻⁷ electroluminescence,⁸⁻⁹ optical pumping,¹⁰ photodetectors,¹¹⁻¹⁷ and field-effect transistors¹⁸⁻¹⁹, energy storage²⁰. The fundamental properties of perovskite materials are determined mainly by band energy engineering, film morphology, crystallinity, defects, dimensionality and surface properties.²¹⁻³⁰ By virtue of extensive materials and device engineering over the last few years, significant progress has been made in perovskite-based optoelectronic devices. In particular, hybrid perovskites are highly attractive for use in light emitting diodes (LEDs) owing to their high color purity, photoluminescence quantum yield (PLQY), external quantum efficiency (EQE), and tunable band gap.

Low-dimensional perovskite and its derivatives are promising materials for light-emitting applications. Compared to their 3D counterpart, charge carriers in low-dimensional perovskite derivatives are confined to the extremely narrow active layers isolated dielectrically from one another by a long organic spacer. This layered or isolated nature of the compounds gives rise to the large exciton binding energies and quantum confinement, promoting fast radiative carrier recombination which is favorable for efficient light-emitting applications. However, breaking up the 3D metal-halide perovskite network into 2D sheets, 1D rods, and 0D isolated clusters using long alkyl (or aryl) ammonium ligands makes them chemically vulnerable because ammonium cations are intrinsically unstable against moisture. Deprotonation of the alkylammonium in water initiates the degradation process of the hybrid perovskites.³¹⁻³² Moreover, theoretical calculations

without considering solvents and oxygen effects suggest that hybrid perovskite materials are intrinsically unstable because of their low Madelung electrostatic potential.³²⁻³³ Therefore, compared with alkyl ammonium cation based perovskites, all inorganic perovskites such as cesium lead halide (CsPbX_3) exhibit improved stability against moisture.³⁴⁻³⁵ Although CsPbX_3 perovskites have better moisture stability than hybrid perovskites, the strong ionic nature of cesium lead halide perovskites still gives rise to chemical instability against polar solvents like water.³⁶ Therefore, the moisture-induced instability is still a ubiquitous impediment for most perovskite materials regardless of the nature of cations or halides.

Here we demonstrate that introducing water on 3D cesium lead bromide (CsPbBr_3) films leads to a direct transformation to highly emissive and thermally stable 2D CsPb_2Br_5 perovskite-related material (PRM) films. The water-induced transformation is governed by a sequential dissolution-recrystallization process under PbBr_2 rich conditions. We find that the post-synthesized 2D PRM films exhibit excellent stability against humidity and high photoluminescence quantum yield up to 29.6% in solid films. Surprisingly, the 2D PRM films show excellent thermal stability as well and do not lose their strong emission even after annealing at 80 °C for 24 hours in air at 65% relative humidity (RH). Our new transformation method provides a robust strategy for generating 2D PRM films without utilizing any alkylammonium cations or ligands as well as rationally tuning optical properties.

Methods

Reagents. Cesium (I) Acetate (CsOAc , Sigma Aldrich), and lead (II) bromide (PbBr_2 , Sigma Aldrich), and lead (II) chloride (PbCl_2 , Sigma Aldrich) were used as received without further purification.

Preparation of CsPbBr₃ and CsPb₂Br₅ films. The precursor solution was prepared by dissolving 1 M CsOAc and 2 M PbBr₂ in DMSO separately. The solutions were heated until they are fully dissolved. 0.5 ml of each CsOAc and PbBr₂ solutions and 0.5 ml of DMF was mixed and used for film preparation. Before film deposition, all glass substrates were cleaned in acetone and isopropanol for 10 min by sonication. The substrates were oxygen-plasma cleaned for 3 min to obtain required hydrophilicity for the uniform spread of drop-casted solution over the substrate. The CsPbBr₃ perovskite films were prepared by simple drop-casting of 80 μ l of precursor solution on the glass substrates while heating the substrates at 80 °C, and the substrates were annealed at the same temperature for 10 min. Different water treatment processes were applied to the CsPbBr₃ films to convert them more emissive CsPb₂Br₅ phase. Simple drop-casting of water or water vapor was employed on top of the perovskite films for transformation. To make more uniform film we left the film in a humidity chamber with 90 % relative humidity (RH) and waited until the CsPbBr₃ converts completely to CsPb₂Br₅. The same procedures were performed for fabrication of CsPb₂Br_{5(1-x)}Cl_{5x} films.

Characterization. *Temperature-dependent (TD) and ambient X-ray diffraction (XRD):* The powder X-ray diffraction pattern was collected using Bruker AXS D8 diffractometer.

Photoluminescence (PL), photoluminescence quantum yield (PLQY): The steady-state PL and PLQY were analyzed using Edinburgh Instruments FLS920 Spectrophotometer with an integrated sphere by excitation at 440 nm wavelength. The PLQY, defined as the percentage of photons emitted over photons absorbed by the sample, was determined by using an integrating sphere. A direct and an indirect measurement were performed to measure PLQY accurately. The re-excitation of the sample from excitation light reflected within the sphere was removed to get accurate results.³⁷

Time-resolved photoluminescence (TRPL) and Temperature-dependent PL (TDPL): Time-resolved photoluminescence was performed using an Ultrafast Systems HALCYONE fluorescence spectrometer with 490 nm excitation wavelength. The temperature-dependent photoluminescence was measured using a Horiba JY LabRAM Aramis spectrometer with an Olympus 50x lens in a Linkam THMS600 stage. A 473 nm laser was used as the excitation source.

Fourier-Transform Infra-Red Spectroscopy (FT-IR): FT-IR measurement was carried out using Thermo Scientific Nicolet 6700 FT-IR spectrometer.

The steady-state Absorption: The steady-state reflection spectra were recorded using Edinburgh Instruments FLS920 Spectrophotometer with an integrating sphere. Then Kubelka-Munk^{6, 38} relation was utilized to convert the reflectance spectra to absorption spectra.

Scanning electron microscopy (SEM): A Quanta 200 FEG instrument was used to obtain SEM images.

Transmission electron microscopy (TEM): TEM analysis was carried out with a Titan TEM (FEI Company) operating at a beam energy of 300 keV and equipped with a Tridiem postcolumn energy filter (Gatan, IQD.). The powder of CsPb₂Br₅ is scratched from film and dispersed in toluene to prepare the TEM sample.

Results and discussion

Direct transformation of 3D CsPbBr₃ films to 2D CsPb₂Br₅ by water treatment.

We employed water to produce stable CsPb₂Br₅ films from CsPbBr₃. Figure 1a illustrates a simple water treatment process. Water dropped directly on the CsPbBr₃ film, and then the film

was annealed at 100 °C for 5 min to dry water. Figure 1b shows water treated films under room light and UV (365 nm) irradiation. The white color area under room light emits green light under UV irradiation. In addition to the direct water dropping method, we also used water vapor using the humidity chamber (90% RH, RT) and observed that the CsPbBr₃ films become emissive. We find that the resulting emissive product is CsPb₂Br₅ as examined below.

The CsPbBr₃ films were fabricated by drop casting of CsOAc:PbBr₂ (1:2) in DMF:DMSO (1:2) solution on glass substrates and annealed at 80 °C for 10 min in air. As illustrated in Figure 1c, CsPbBr₃ has a simple cubic structure with corner sharing PbBr₆⁴⁻ octahedra. In contrast, the transformed tetragonal CsPb₂Br₅ has a unique sandwiched structure with alternating (Pb₂Br₅)⁻ and Cs⁺ layers.

The water-induced transformation can take place with a two-step process under PbBr₂ rich condition. As an initial step, water accelerates the removal of Cs⁺ ions from CsPbBr₃, which causes the irreversible decomposition of perovskites generating PbBr₂, Cs⁺ (aq) and Br⁻ (aq). This is because of the high solubility of CsBr in water and strong ionic nature of CsPbBr₃. In a PbBr₂ rich condition such as 1:2 molar ratio of CsOAc and PbBr₂, tetragonal CsPb₂Br₅ can be obtained by the recrystallization process in water through the anisotropic growth of 2D CsPb₂Br₅ which is a thermodynamically favorable state at given stoichiometric ratio with the existence of water. Since water can dissolve CsPbBr₃ immediately, this transition is completed nearly within 1 min after all water molecules are evaporated by thermal annealing (See video in supporting information). Evaporation of water molecules was monitored by measuring infrared spectroscopy of the samples before and after water treatment and thermal annealing. As shown in Figure 2, the broad OH stretching vibration of water molecule around 3300 cm⁻¹ is disappeared after thermal annealing at 100 °C for 5min.

Next, we examined how stoichiometry affects the crystal structure. With 1:1 and 2:1 molar ratios of CsOAc:PbBr₂, we were not able to observe strong green emission after water treatment because of inefficient phase transformations with stoichiometric imbalance (Figure S1). The highest transformation level into CsPb₂Br₅ was achieved with a 1:2 ratio according to the XRD peak intensity at 11.6° (almost 2.5 times that of materials synthesized with a 1:1 ratio and much higher than those using a 2:1 ratio) (Figure S1c), which corresponds to the (002) plane of the phase. This is in good agreement with previous reports on the formation of CsPb₂Br₅ with the excess of PbBr₂ under thermal annealing, and further supported by the calculation of reaction probability with the Gibbs free energy of CsPbBr₃, PbBr₂, and CsPb₂Br₅.³⁹

Figure 3b shows the X-ray diffraction (XRD) patterns of the original CsPbBr₃, transformed CsPb₂Br₅ by water treatment, and after thermal annealing at 80 °C for 24 hours. The XRD result clearly shows that the cubic CsPbBr₃ are converted to the tetragonal CsPb₂Br₅ after water treatment. The (002) plane of the tetragonal CsPb₂Br₅ at 11.6° shows domination over the remaining small peaks of 3D CsPbBr₃. Note that the transformed CsPb₂Br₅ films are highly stable, i.e., maintaining the tetragonal XRD pattern even after thermal annealing at 80 °C for 24 hours in the air. Also, the XRD after humidification of the film does not change after annealing (Figure S2), it shows the conversion occurs independent to heating. More interestingly, the strong green emission from the transformed CsPb₂Br₅ films is not quenched by thermal annealing in air for 24 hours (Figure 3a). These results clearly show that the transformed CsPb₂Br₅ films possess good thermal stability. We further examined its thermal stability by measuring XRD from 303 K to 583 K and found that there is a negligible change in XRD patterns up to 563 K (Figure S3).

To get a deeper understanding of water induced transformation process, we performed a detailed analysis of absorption spectra under the phase transformation from CsPbBr_3 to CsPb_2Br_5 . Figure 4a shows the absorption spectra upon the exposure time of CsPbBr_3 films on water vapor generated from a humidifier. By water vapor treatment for 40 seconds, the absorption across the spectral range of 370-550 nm decreases immediately due to the dissolution (or decomposition) of CsPbBr_3 . At 40 seconds, a new peak at 370 nm was emerged and become more and more distinct by further water vapor treatment. In the range of 150-220 seconds, another absorption peak around 390 nm was generated and disappeared after 220 seconds. We postulate that this peak could be assigned to $(\text{Pb}_2\text{Br}_5)^-$ intermediates. For structural investigation, scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) were used. The transformed CsPb_2Br_5 film's morphology could be seen in the SEM micrograph in Figure S4a. The HRTEM images in Figures S4b and c reveal interplanar distances of about 0.42 nm and 0.38 nm, which could be assigned to the (020) and (004) planes, respectively. The HRTEM results are in good match with the XRD results. Figure 4b clearly shows the difference of absorption spectra between CsPbBr_3 and CsPb_2Br_5 . The band gap of 3.35 eV estimated from the absorption edge of CsPb_2Br_5 films is in good agreement with the previously reported values from CsPb_2Br_5 single crystals.⁴⁰

Figure 4c shows the photoluminescence spectra of as-prepared CsPbBr_3 , transformed CsPb_2Br_5 and annealed CsPb_2Br_5 films. The PL emission spectra show that the maximum PL peaks at 527 nm for CsPbBr_3 and 532 nm for both transformed and annealed CsPb_2Br_5 films. A high PLQY of 29.6% was observed from the solid films of CsPb_2Br_5 with the excitation wavelength of 440 nm (Figure S5). This PLQY value is relatively higher than that of generally reported values from CsPbBr_3 colloidal nanocrystals. The relatively high PLQY, especially in solid films, from the

transformed CsPb₂Br₅ is because there is no aggregation induced PL quenching in solid state and loss of ligands by thermal annealing or oxidation with water. In addition, the time-resolved PL measurement was carried out on the transformed CsPb₂Br₅ films to characterize carrier recombination dynamics. The PL decay of CsPb₂Br₅ shows a single exponential decay profile with a lifetime of 50.4 ns (Figure 4d). By using PLQY and average lifetime with the basic equations ($k_r = \Phi/\tau_{ave.}$ and $k_{nr} = (1 - \Phi)/\tau_{ave.}$, where Φ is the PLQY, and $\tau_{ave.}$ is the average PL lifetime), we estimated the radiative (k_r) decay rate of 0.0059 ns⁻¹ and nonradiative (k_{nr}) decay rates of 0.014 ns⁻¹.

To get a better insight into the excitonic features of the transformed CsPb₂Br₅ films and correlate it with the PL properties, we measured TD-PL spectra of the CsPb₂Br₅ films (Figure 5a). The increase of temperature leads to the small blue shift of PL peaks from 532 to 527 nm and the decrease of PL intensity (Figure 5b) with increasing a full width at half maximum (FWHM) (Figure 5c). The blue shift of PL peaks can be interpreted with thermal expansion of the crystal lattice and the electron-phonon coupling.⁴¹⁻⁴³ The spectral linewidth broadening with increasing temperature may arise from charge-carrier interactions with optical phonons during the carrier recombination process.^{41, 44} To estimate the exciton binding energy of the transformed CsPb₂Br₅ films, the TD- PL intensity curve was fitted by using the equation: $I(T) = I_0/(1 + A\exp(E_b/k_B T))$, where I_0 is the estimated integrated PL intensity at 0 °K, k_B is the Boltzmann constant, and E_b is the exciton binding energy. An E_b of 99.7 ± 12.4 meV was estimated for CsPb₂Br₅ films, which is higher than that of previously reported values for CsPbBr₃ (30~50 meV).⁴⁵⁻⁴⁶ This high exciton binding energy reveals that the spatially distinguished electronic states of the transformed CsPb₂Br₅ play a significant role in the absorption and emission process.

In addition to the CsPb_2Br_5 , we also examined the structural evolution of the other halide composition of $\text{CsPb}_2\text{Br}_{5(1-x)}\text{Cl}_{5x}$. Optical emission spectra of layered structure can be tuned from green to blue (Figure 6a) by adjusting the ratio of chloride to bromide. The PL peak position was blue shifted to 473 nm for $x=0.37$. The XRD patterns with different ratios of chloride (Figure 6b) show that the layered structure is mostly maintained in the tetragonal phase. As expected, upon incorporation of Cl^- the XRD peak for (002) plane (Figure S6) shifts to higher 2θ angles by shrinkage of the lattice constant.

Overall, we demonstrated that water-induced dimensionality transformation could be a powerful strategy for generating emissive 2D PRMs. However, care must be taken before generalizing our results because the origin of the green emission from the CsPb_2Br_5 is still obscure. Recent reports including from our group revealed that CsPb_2Br_5 single crystals⁴⁰ and nanosheets³⁹ (in their ideal intrinsic forms) are PL inactive because they are indirect band gap materials. However, several reports are showing that CsPb_2Br_5 nanoplates have a strong green emission and also exhibit low-threshold amplified spontaneous emission.⁴⁷⁻⁴⁸ One plausible hypothesis is that small amounts of embedded CsPbBr_3 crystals in CsPb_2Br_5 materials maybe the source of the green emission. However, our excitation wavelength-dependent emission intensity spectral maps reveal that the maximum PL comes from a clear excitation peak around 370 nm, which is close band edge of CsPb_2Br_5 as shown in Figure S7b. This means that the majority of green emission has a strong correlation with the transformed CsPb_2Br_5 . Essentially, lattice strain typically exists in nano-scale materials, which could influence the band structure of indirect band gap materials. In addition, dissolution-recrystallization processes caused by water might initiate the formation of emissive centers which could be possibly generated by defects or surface states in PRMs.^{28-29, 49-53} It is well known that surface defects can be easily generated by oxygen or

moisture induced reorientation of crystal structure or decomposition. Indeed, we also observed that PL inactive CsPb_2Br_5 *single crystals* turn green photoluminescent after prolonged exposure to a humid atmosphere (Figure S8). Accordingly, for our transformed CsPb_2Br_5 films the presence of emissive centers such as the surface states and defects located inside the CsPb_2Br_5 crystals as well as at the surface generated by water treatment might be correlated with the emission properties of the CsPb_2Br_5 . Detailed structural analysis on this material will be the subject of our future work.

Conclusion

In summary, the fast degradation of perovskites in the presence of water and moisture is a challenge for perovskite-based technologies and hinders the material's potential. In this work, we demonstrate that water can be a useful tool for the direct transformation of three-dimensional perovskites (CsPbBr_3) into the 2D PRM CsPb_2Br_5 . We revealed that our transformed 2D PRM film is a good green emissive optical medium exhibiting high thermal and environmental stabilities. The transformation occurs by a sequential dissolution-recrystallization process under the PbBr_2 rich condition. We believe our finding is significant to perovskite technologies because it not only provides a new synthetic method to increase the moisture stability but also presents a vital strategy for obtaining highly emissive PRMs. The new developed water-induced direct transformation method will have an impact on the stabilization of PRMs for light-emitting applications.

ASSOCIATED CONTENT

Supporting Information. TD-XRD, SEM images, TEM images, PLQY, excitation wavelength dependent PL intensity, XRD of CsPb₂Br₅ with different ratio of chloride are included in Supporting Information.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Figure 1. (a) Schematic representation of the water induced direct transformation of CsPbBr_3 to CsPb_2Br_5 . (b) Photographic image of water treated films under room light and UV light. (c) The structure of cubic CsPbBr_3 and tetragonal CsPb_2Br_5 .

Figure 2. FT-IR spectra of CsPbBr₃, the transformed CsPb₂Br₅ before and after annealing for 5 min and 30 min at 100°C. The broad water peak (red line) observed from 3000 to 3600 cm⁻¹ was disappeared after thermal annealing.

Figure 3. (a) Photographic images of CsPbBr₃ films after drop casting (top), transformation to CsPb₂Br₅ by water vapor treatment (middle), and annealing at 80 °C for 24h (bottom). (b) XRD of CsPbBr₃ (before transformation), the transformed CsPb₂Br₅ film and after annealing 80 °C for 24h.

Figure 4. (a) The evolution of absorption spectra depending on the exposure time of CsPbBr₃ films on water vapor. (b) The absorption spectra of CsPbBr₃ film before and after water vapor treatment for 340 sec. (c) PL spectra of CsPbBr₃, transformed CsPb₂Br₅, and after annealing for 24h at 80 °C in air. (d) Time-resolved PL spectrum of the transformed CsPb₂Br₅ film with an excitation wavelength of 490 nm.

Figure 5. (a) Temperature-dependent PL spectra of transformed CsPb_2Br_5 in the range of 93-293 °K. (b) The integrated PL intensity and (c) full-width and half maxima (FWHM) versus temperature.

Figure 6. (a) PL spectra of $\text{CsPb}_2\text{Br}_{5(1-x)}\text{Cl}_{5x}$ films. Inset shows the photographic image of transformed films under UV irradiation. (b) XRD of $\text{CsPb}_2\text{Br}_{5(1-x)}\text{Cl}_{5x}$ films with different ratio of chloride.

TOC Graphic