CsPbBr₃ Perovskite Powder, a Robust and Mass-Producible Single-Source Precursor: Synthesis, Characterization, and Optoelectronic Applications

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Supporting Information

ABSTRACT: A facile synthesis method is proposed for the mass production of high-quality CsPbBr₃ perovskite powder. It is shown that the proposed synthesis protocol is capable of producing polycrystalline CsPbBr₃ powder in quantities greater than 10 g. The derived thin films by thermal evaporation and spin-coating are of compact morphologies (root-mean-square roughness ≪ 4 nm) without voids and pinholes. Moreover, the thin films show obvious photoluminescence (PL) with a narrow (bandwidth ≪ 19 nm) peak centered at ~520 nm, which is blue-shifted compared with the PL emission of the powder at 542 nm. The powder and the spin-coated film exhibit superior PL stability under long-term ambient conditions and in thermal cycling experiments performed at temperatures up to ~120 °C. Accordingly, optoelectronic applications including the fabrication and characteristics of the electroluminescence device, the organic–inorganic powder doped with methylammonium and formamidinium ions, and fluorescent greenish-blue quantum dots are also demonstrated. On the basis of these demonstrations, the synthesized CsPbBr₃ perovskite powder can be expected to empower the advances in perovskite-related optoelectronics in the future.

1. INTRODUCTION

Since the discovery of facile synthesis and potential optoelectronic applications in 2009,¹ lead halide perovskites have become the subject of intense research worldwide for their prowess in versatile synthesis and record-breaking device performance, colloidal nanocrystal or quantum dot (QD) synthesis,² nanocrystal pinning or vapor treatment for performance, colloidal nanocrystal or quantum dot (QD) deposition,³,⁴ solar cells with certified power conversion efficiency of 23.3%,⁵ and green CsPbBr₃ light-emitting diodes (LEDs) with an ultrahigh luminance over 590 000 cd/m²⁶ to name a few. Despite these astonishing success and achievements, it is well-known that poor stability is the key issue to hinder halide perovskites from practical commercialization.⁷ To overcome this drawback, cesium cations were introduced to replace the organic part, ammonium (MA) CH₃NH₃⁺ or formamidinium (FA) CH(NH₂)₂⁺, in hybrid lead halides, and indeed, all-inorganic systems show higher thermal stability and thus better device reliability.⁵,⁸ Similarly, sodium and tin were proposed to partially substitute MA and lead cations, respectively, in halide perovskites to improve the long-term stability of the device.⁹,¹¹

To deposit a lead halide film, a most popular form for optoelectronic applications, MAX, FAX, or CsX (X denotes the halogen) is typically used as the source of large cations to be mixed with PbX₂, the source of small cations, in peculiar protic solvent to form the precursor solution based on the simple one-step method. With a specific treatment or polymer addition, the starting precursor solution is compatible for accessing a smooth film on substrates by any solution process.²–⁵ However, the exact molar ratio of the monovalent large cations (MA⁺, FA⁺, or Cs⁺) to the Pb cation in precursors is crucial and not as straightforward as the stoichiometric ratio in ABX₃ halide perovskites. For instance, the ratio of MAX or CsX to PbX₂ larger than 1.0 even 2.0 is frequently adopted to prevent the formation of impurity phases (ex: excess Pb metal or residual PbX₂), which probably cause the exciton quenching in devices.⁶–⁹ Therefore, when the precursor solutions are used for solid thin-film preparation, those unreacted and non-coordinating precursors are deposited as well and irremovable via any post-deposited treatments, no matter the simple one-step or sophisticated two-step coating methods are used.¹² Being an alternative, Hoffman et al. successfully obtained the continuous and smooth CsPbBr₃ films by fusing the purified perovskite nanocrystals coated on TiO₂ films at 250 °C.¹³ However, the thermal treatment entirely caused the photoluminescence (PL) quenching of the annealed CsPbBr₃ film. As a consequence, not only the optical and electrical but also the structural properties such as morphology, crystal grain size, and crystallinity of the thin films are affected.

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In the present study, we demonstrated the facile synthesis of CsPbBr₃ powder by dropping hydrohalic acid into the CsBr and PbBr₂ solution at room temperature. By further precipitation-redispersion procedure, those excess unreactants can thus be removed. In this way, the synthesis of CsPbBr₃ powder is capable for mass production for optoelectronics industry. From the PL measurement, we found that not only the CsPbBr₃ powder but also the hereby spin-coated thin film are highly stable in ambient air and after thermal stress at temperature higher than 120 °C.

2. EXPERIMENTAL SECTION

2.1. Synthesis of CsPbBr₃ Powder. To synthesize the CsPbBr₃ powder, 1.9 mmol PbBr₂ and CsBr were added in 3 mL of dimethyl sulfoxide (DMSO) and the solution was vigorously stirred for 30 min. Subsequently, 3 mL of hydrobromic acid (HBr) was added dropwise into the transparent solution with continuous stirring and the orange turbid solution was immediately observed indicating the formation of CsPbBr₃. In fact, HBr was also reported to be added in the precursor solution to reduce the voids and pinholes of the spin-coated MAPbBr₃ films. After centrifuging the solution and discarding the supernatant, the precipitate was washed twice by adding certain amount of ethanol to remove unreacted agents. Finally, orange CsPbBr₃ precipitate was washed twice by adding certain amount of ethanol to remove unreacted agents. Finally, orange CsPbBr₃ precipitate was washed twice by adding certain amount of ethanol to remove unreacted agents.

2.2. Film Deposition. The dry CsPbBr₃ powder was then subjected to film deposition. By thermal evaporation at 5 × 10⁻⁶ Torr, a high-quality film with the thickness exceeding 100 nm can be readily deposited on various substrates such as silicon or indium–tin–oxide (ITO)/glass. Also, 290 mg (0.5 mmol) of the CsPbBr₃ powder precursor was dissolved in 1.5 mL of DMSO for film deposition by solution process. It should be mentioned that unlike those strongly emissive CsPbBr₃ nanocrystals dispersed in hexane or toluene, our CsPbBr₃ DMSO solution is colorless and transparent under normal light irradiation (see Figure S2). Poly(ethylene oxide) (PEO) was then added into the solution in the weight ratio of CsPbBr₃/PEO = 1:0.07, from which the yellowish CsPbBr₃ films can be obtained by spin-coating at 3000 rpm for 80 s and baking at 60 °C for 30 min on substrates pretreated with O₂ plasma.

2.3. Synthesis of CsPbBr₃ QDs. To synthesize the CsPbBr₃ QDs, 0.2 mmol CsPbBr₃ powder was mixed with 0.25 mL of oleylamine and 0.5 mL of oleic acid in 5 mL of dimethylformamide under stirring at 60 °C for 3 h to completely dissolve the powder. After cooling down to room temperature, 1 mL of the precursor solution was injected into 10 mL of toluene to obtain the well-dispersed QDs.

3. RESULTS AND DISCUSSION

3.1. Characterization of CsPbBr₃ Powder and Films. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of the perovskite powder are shown in Figure 1. The abrupt weight loss at 214 °C should be attributed to the ignition of DMSO or its related complex because of the exothermic peak shown in the DTA curve. Very low weight loss of ~0.17% at this stage indicates that twice washing by ethanol is sufficient to remove DMSO residues in the produced powder. The onset of decomposition is at ~510 °C because of the evaporation of PbBr₂, and the obvious weight loss at ~568 °C is due to the melting of powder. The high-temperature sustainability of the powder is also a unique merit to remove those unremovable impurities by precipitation purification during synthesis. As shown, the weight loss is only 5.8% of its original weight as the temperature increases to 600 °C, indicating the high thermal stability of CsPbBr₃.

From the scanning electron microscopy (SEM) image shown in the inset of Figure 2, the CsPbBr₃ powder comprised tetragonal-shaped microcrystals with sizes ranging from a few to tens of micrometers. The X-ray diffraction (XRD) patterns of the synthesized powder and evaporated and spin-coated films are presented in Figure 2. The peaks at 2θ = 21.52°, 26.36°, 30.40°, 30.72°, and 34.37° are in good agreement with diffractions from (020), (022), (004), (220), and (222) planes of orthorhombic polycrystalline CsPbBr₃ perovskite which features the splitting peaks at 30°–31°, without detectable secondary phases such as PbBr₂ and PEO. It indicates that the synthesis powder and hereby derived thin films are high-quality CsPbBr₃ polycrystals and inherit the superior properties widely reported in general. More specifically, from the total X-ray photoelectron spectroscopy (XPS) spectrum of the as-synthesized powder shown in Figure S3a, the molar ratio of incorporated Cs₃, Pb, and Br elements is 1:0.98:3.05, highly close to the ideal stoichiometry of CsPbBr₃.
residues of DMSO and ethanol. In the Pb 4f core-level spectrum (Figure S3b), the peak corresponding to 4f7/2 is centered at \( \sim 138 \text{ eV} \) and no obvious signal was detected in the energy range for metal Pb\(^{18,19} \), which means the peak is mainly associated with the stoichiometric CsPbBr\(_3\).

As shown in Figure 3, the optical absorption spectra of the spin-coated and evaporated films exhibit a distinct absorption peak at 515 and 516 nm, respectively, while the strong excitonic emission peaks at 519 and 522 nm with narrow full width at half-maximum (fwhm) of 17.6 and 18.9 nm are depicted in the PL spectra. The nominal shift of the absorption peak for the evaporated film compared to that of the spin-coated film maybe attributed to the small discrepancy of crystal grain sizes and uniformity,\(^{20} \) which also results in the shift of the PL peak. The band gap energy of 2.356 and 2.360 eV is thus determined for the evaporated and spin-coated films from the transformed Kubelka–Munk function (see Figure S4).\(^{21,22} \) The PL spectrum of the powder is also shown for comparison of the peak shift. Considering the weaker PL intensity of the powder compared to that of the thin film, the large blue shift of PL peak position is probably a result of defect-related exciton emission in the powder.\(^{23} \)

For lead halide perovskites, the deposition of a smooth and continuous thin film for optoelectronic applications is always challenging and never being straightforward, as the homogeneous and even morphology is the essential factor toward efficient device applications. The topographical atomic force microscopy (AFM) images of the evaporated and spin-coated thin films are measured and shown in Figure 4. The root-mean-square (rms) roughnesses of the evaporated and spin-coated films on Si substrates and the spin-coated ones on the ITO/glass substrate are 3.5, 2.9, and 3.1 nm, respectively, which is homogeneous and smooth enough for most optoelectronic devices. As shown, small and uniform crystalline grains can be obtained by thermal evaporation with the deposition rate lower than 0.2 Å/s. Despite the similar grain size shown in Figure 4b,c, the slight rougher surface of CsPbBr\(_3\) films spin-coated on ITO/glass should be attributed to the roughness (\( \sim 5 \text{ nm} \)) of underneath ITO films.\(^{24} \) Except the minor voids of spin-coated films on ITO/glass, no pin holes responsible for leading electrical short are found in all deposited films. The thickness of both evaporated and spin-coated films was determined as \( \sim 114 \text{ nm} \) by scratching a part of the film to create the difference of height (see Figure S3).

### 3.2. Air Stability

As shown in Figure 5, the air stability of the CsPbBr\(_3\) powder on an Al foil and the spin-coated film on the Si substrate were evaluated by recording the long-term PL intensity of samples exposing in an ambient environment at 25 °C and with 50–70% relative humidity. It should be mentioned that the air exposure time-dependent PL intensity of the evaporated film was not measured because of its less PL efficiency under the irradiation of a UV (\( \lambda \approx 400 \text{ nm} \)) LED, the excitation source. Therefore, the characteristics of the measured film in the following discussion solely referred to those of the spin-coated film. In Figure 5, PL intensities exceeding 83% of the original value from the powder can be retained for up to \( \sim 100 \text{ h} \). Though the intensity seems to slowly increase after \( \sim 70 \text{ h} \), the fluctuation is not as significant as that from the film which rapidly increases to >140% within the Si substrate were evaluated by recording the long-term PL intensity of samples exposing in an ambient environment at 25 °C and with 50–70% relative humidity. It should be mentioned that the air exposure time-dependent PL intensity of the evaporated film was not measured because of its less PL efficiency under the irradiation of a UV (\( \lambda \approx 400 \text{ nm} \)) LED, the excitation source. Therefore, the characteristics of the measured film in the following discussion solely referred to those of the spin-coated film. In Figure 5, PL intensities exceeding 83% of the original value from the powder can be retained for up to \( \sim 100 \text{ h} \). Though the intensity seems to slowly increase after \( \sim 70 \text{ h} \), the fluctuation is not as significant as that from the film which rapidly increases to >140% within the Si substrate were evaluated by recording the long-term PL intensity of samples exposing in an ambient environment at 25 °C and with 50–70% relative humidity. It should be mentioned that the air exposure time-dependent PL intensity of the evaporated film was not measured because of its less PL efficiency under the irradiation of a UV (\( \lambda \approx 400 \text{ nm} \)) LED, the excitation source. Therefore, the characteristics of the measured film in the following discussion solely referred to those of the spin-coated film. In Figure 5, PL intensities exceeding 83% of the original value from the powder can be retained for up to \( \sim 100 \text{ h} \). Though the intensity seems to slowly increase after \( \sim 70 \text{ h} \), the fluctuation is not as significant as that from the film which rapidly increases to >140% within

![Figure 3. Optical absorption and PL spectra of the CsPbBr\(_3\) powder and the derived evaporated and spin-coated films. Inset is an image of the CsPbBr\(_3\) powder under UV irradiation.](image-url)

![Figure 4. AFM images of (a) evaporated and (b) spin-coated CsPbBr\(_3\) films on silicon substrates and (c) spin-coated one on the ITO/glass substrate. The scale bar represents 1 μm.](image-url)

![Figure 5. PL intensity ratio of CsPbBr\(_3\) powder and spin-coated film as a function of air exposure time.](image-url)
1.5 h and becomes ~198% after 100 h. The discrepancy of these results can be explained by the prepared sample condition for analysis. The powder was pressed to be a thick film with a thickness over 300 μm, whereas the thickness of a spin-coated film is only about 100 nm. That is, the effect of air exposure is quickly responded in the thin spin-coated film, whereas most of the beneath powder does not directly expose to the air and the measured PL only shows the ensemble result. On the basis of this demonstration, the CsPbBr3 powder and spin-coated film are immune to environmental degradation from air and moisture and can be directly exposed in ambient air for several days at least. On the other hand, the increase of PL intensity with the increase of air exposure time has been reported in the printed 3–4 μm-thick MAPbBr3/PEO composite film and the authors directly related this phenomenon to the efficiency improvement of derived perovskite LEDs.25 On the basis of the increase of PL lifetime, the authors attributed the PL enhancement by air exposure to the decrease of defect density due to self-healing of the perovskite lattice upon moisture.

3.3. Thermal Stability. The thermal stability of the powder and spin-coated film was also evaluated by recording the PL intensity in thermal cycling experiments. To avoid the influence of air and moisture exposure, samples were heated on a hotplate in a nitrogen-filled glovebox with both oxygen and moisture concentration at ≤1 ppm. As shown in Figure 6, the measurement begins at 30 °C and the temperature is increased to 120 or 140 °C and then decreased to 30 °C. As the temperature elevates, the PL intensity of the powder gradually reduced to 90% at 140 °C because of the thermal quenching effect. Noticeably, the subsequent decrease of temperature does not significantly recover the PL intensity, consistent with the observation in alkyl-phosphate-coated CsPbBr3 QDs by Xuan et al.26 Unlike organic and inorganic lead halide nanocrystals undergoing severe PL quenching due to thermally assisted defect trapping, phase transition, or structural decomposition at high temperatures,27,28 the CsPbBr3 powder exhibits the much stable thermal stability, even though the irreversible PL intensity. In the present research, the color and lattice structure of the powder do not have apparent difference after thermal stressing. Therefore, the superior thermal stability of the pristine CsPbBr3 powder without sophisticated decoration or treatment should be attributed to the reduction of nonradiative defects and impurities via purification in the synthesis procedure.

For the CsPbBr3 film, a very different variation of PL intensity was observed. With increasing temperature, the intensity initially increases at temperatures below 90 °C and rapidly decreases to 58% at 120 °C. The initial intensity improvement of PL intensity at temperatures below 90 °C can be simply explained as the annealing effect, and the thermal quenching effect influences the PL when the temperature continues to increase. The observed variation well explains that the typical annealing temperature for the CsPbBr3 films is below 100 °C. Later, in the process of cooling down to room temperature, the remarkable enhancement of PL intensities beyond the initial values was recorded. Being a possible interpretation, it was reported that the existence of second-phase CsPb2Br5 during the synthesis of CsPbBr3 QDs could be beneficial for the device fabrication.29 With a higher amount of halogen atoms, the CsPb2Br5 near the crystal grain boundary could prevent the excitons being trapped by the defects (the so-called self-passivation effect), and optoelectronic devices with higher efficiency could thus be achieved. Therefore, the thermally induced phase transition from CsPbBr3 to CsPb2Br5 might be responsible for the observed PL enhancement of spin-coated CsPbBr3 film during cooling. However, from the XRD spectra of the samples before and after thermal stress (see Figure S6), no apparent difference is detected probably because of a small amount of CsPb2Br5 crystal.

3.4. Fabrication and Characterization of EL Devices. On the basis of the above results, the deposition conditions of the spin-coated CsPbBr3 films were then applied to fabricate the electroluminescence (EL) devices. The device structure can be simply described as ITO/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PE-DOT:PSS)/CsPbBr3/2,2’,2’’-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi)/Ca/Al where the spin-coated PEDOT:PSS (Clevios P VP 4083) and thermally evaporated TPBi (E-Ray Optoelectronics Technology Co.) served for hole injection and electron transporting, respectively. The luminance–current density–voltage (L–J–V) curves of the EL device are shown in Figure 7. As shown, a very low light turn-on voltage of about 3.3 V is observed accompanying with the maximum luminance of ~3700 cd/m2 at 8.0 V. From the difference of current turn-on (2.3 V) to light turn-on (3.3 V) voltages, it is anticipated that the device performance can be further improved by inserting a hole-transport layer such as poly(N,N’-bis(4-butylphenyl))-N,N’-bis(phenyl)benzidine) or

![Figure 6](image_url)

**Figure 6.** Variation of PL intensity ratio of CsPbBr3 powder and spin-coated film with measurement temperature. Arrows indicate the testing sequence.

![Figure 7](image_url)

**Figure 7.** L–J–V characteristics of EL device derived from perovskite powder. Inset is the comparison of normalized PL and EL spectra.
poly(9,9′-dioctyfluorene-co-N-(4-butylphenyl)diphenyl amine). In the inset of Figure 7, the EL spectrum is peaked at 519.5 nm, which is very close to the PL peak at 519 nm. Furthermore, the spectral width of EL spectrum is slightly broadened to 18.4 nm, which is also similar to that of PL spectrum.

3.5. Demonstration of MA-, FA-Doped CsPbBr3 Powder, and CsPbBr3 QDs. Finally, to demonstrate the flexibility of the facile synthesis in this study, partial CsBr precursor was replaced with MABr and FABr in the synthesis procedure to produce MA0.3Cs0.7PbBr3 and FA0.3Cs0.7PbBr3 powder. The corresponding XRD patterns are compared with that of pristine CsPbBr3 powder and are shown in Figure 8, and obvious peak shifts to higher angles are observed, indicating the successful incorporation of MA and FA atoms into the lattice. The appearance of MACsPbBr3 and FACsPbBr3 powder is slightly darker than that of CsPbBr3. With the same total molar amount of precursors of large cations (CsBr, MABr, and FABr), the produced MACsPbBr3 and FACsPbBr3 powder is fewer, that is, the molar ratio of large cations to the small cation (PbBr2) has to be optimized in the synthesis of MACsPbBr3 and FACsPbBr3 powder. On the other hand, the CsPbBr3 powder was adopted to replace the CsBr and PbBr2 in the room temperature synthesis of CsPbBr3 QDs based on the protocol previously reported,30 as mentioned in the Experimental Section. However, different to the reported green-emitting QDs, our QDs exhibit strong greenish-blue luminance under UV irradiation as shown in Figure 9. The emission is peaked at 492 nm with a fwhm of 31 nm.

4. CONCLUSIONS

In conclusion, we have demonstrated the facile synthesis and characteristics of CsPbBr3 powder and the evaporated and spin-coated thin films. The produced amount of high-quality CsPbBr3 powder, namely the single-source precursor, can easily exceed 10 g, after twice purification to remove unreactants and unwanted side products. With proper deposition conditions, smooth and continuous films with rms roughnesses below 4 nm can be obtained by thermal evaporation or spin-coating. According to the results of long-term measurement of PL intensity in ambient air, the powder and spin-coated films are very stable without significant PL degradation for ~100 h. Their high thermal stabilities are also demonstrated in the thermal cycling experiment. Finally, the EL device with a spin-coated CsPbBr3 emissive layer exhibits low light turn-on voltage of 3.3 V and a maximum luminance of ~3700 cd/m2. On the basis of these demonstrations, the facile synthesis of purified lead halide perovskite powder is promising and highly viable for next-generation optoelectronics.

■ ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00385.

High-quality CsPbBr3 powder with a total weight of ~12.1 g can be produced in a single synthesis process by increasing the amount of the precursor; photographs of CsPbBr3−PEO−DMSO solution and evaporated and spin-coated CsPbBr3 films; XPS survey scan and Pb 4f core-level spectrum of as-synthesized CsPbBr3 powder; plot of transformed Kubelka–Munk function versus photon energy of incident light for evaporated and spin-coated CsPbBr3 films; AFM film thickness measurements of evaporated film on the Si substrate and spin-coated film on the ITO/glass; and XRD spectra of the CsPbBr3 powder and the spin-coated film before and after thermal stress; inset: photographs of the powder (PDF)

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Notes
The authors declare no competing financial interest.

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