

# High-Quality MAPbBr<sub>3</sub> Cuboid Film with Promising Optoelectronic Properties Prepared by a Hot Methylamine Precursor Approach

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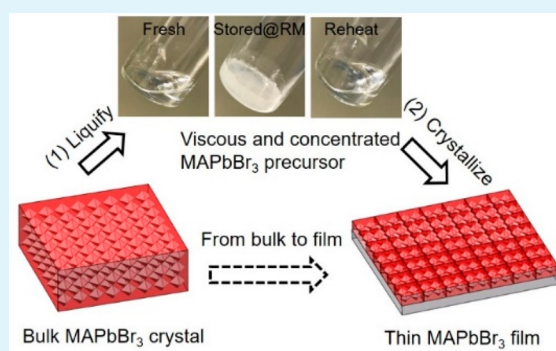
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**ABSTRACT:** Though CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> single crystals are frequently applied in various optoelectronic devices due to their favorable cuboid geometry, superior optoelectronic properties, and better stability than CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> polycrystalline films normally show poorer morphology with scattered crystals than their iodide counterparts, inherently due to their different crystallization habits. In this work, a facile process based on a hot methylamine-based precursor with high viscosity and concentration is demonstrated to counteract rapid ion diffusion. The precursor also has special features including a large colloidal size, a solid form at room temperature, and fast crystallization offered by the easy evacuation of methylamine. CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> films composed of tightly aligned CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> cuboids on micron scale are obtained. Wide channel (100 μm) photodetectors made from the CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> films show promising photoresponse and fast response speeds on par with those based on single crystals, suggesting high film quality and good optoelectronic connections between neighboring cuboids.

**KEYWORDS:** MAPbBr<sub>3</sub> hybrid perovskite, cuboid, single crystals, methylamine, photodetectors, film orientation, mosaic, colloids



## INTRODUCTION

CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> (MAPbBr<sub>3</sub>, where MA = CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>), as one of the typical organic–inorganic halide hybrid perovskite materials, has superior optoelectronic properties and better stability than iodide-based perovskites MAPbI<sub>3</sub>.<sup>1–3</sup> Excellent performances in the detection devices of photons<sup>4–9</sup> and charged particles<sup>10</sup> based on MAPbBr<sub>3</sub> single crystals with favorable cuboid geometry have been frequently reported. Though MAPbBr<sub>3</sub> single crystals generally show less defects compared with polycrystalline films and thus better device performances, it is still a challenging issue to integrate crystals with substrates to form large-area flat-panel devices due to the restrictions in lattice matching and poor compatibility with other functional device layers.<sup>4,11</sup> Obtaining substrate integration with stand-alone single-crystal thin films (SCTF) by slicing bulk perovskite single crystals also presents challenges because of the fragile nature of these materials.<sup>12,13</sup> Therefore, a variety of applications in solar cells,<sup>14–17</sup> light-emitting diodes,<sup>18</sup> and lasers<sup>19</sup> have been based on MAPbBr<sub>3</sub> thin films. Inherently, there is a tendency to form discontinuous MAPbBr<sub>3</sub> crystals scattering on substrates (which could reach microscale distance) when preparing MAPbBr<sub>3</sub> films by conventional methods such as spin-coating and dip-coating, even though these methods yield continuous and high-quality films for MAPbI<sub>3</sub>.<sup>19–25</sup> The presumed reason is that the enhanced growth rate of the perovskite grains results from the higher diffusivity of the smaller bromide ion than the iodide

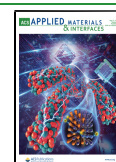
ion.<sup>26,27</sup> There have been efforts to improve MAPbBr<sub>3</sub> film quality by using additives such as PbCl<sub>2</sub>,<sup>20</sup> polyimide,<sup>23</sup> and poly(ethylene oxide),<sup>23,24</sup> which, however, produce issues regarding film impurities and degraded optoelectronic properties. There have also been efforts to grow films with small single crystals by seeding them on substrates, but this leads to a discontinuous appearance with wide gaps (on the scale of micrometers) between the crystals and a concern over substrate attachment.<sup>28</sup> Efforts have been made to grow films by space confinement, but a long growth time and delicate setup are required.<sup>6,17,29</sup> Consequently, it is highly desirable to realize MAPbBr<sub>3</sub> films with simultaneous high quality and well integration with the substrate for unlocking their applications in high-performance optoelectronic devices.

In this work, we propose a method to prepare high-quality and substrate-integrated MAPbBr<sub>3</sub> films consisting of compactly aligned MAPbBr<sub>3</sub> cuboids based on a solvent-free methylamine (CH<sub>3</sub>NH<sub>2</sub>) precursor without any extraneous additives. Taking into account the natural solid-state phase of the precursor at

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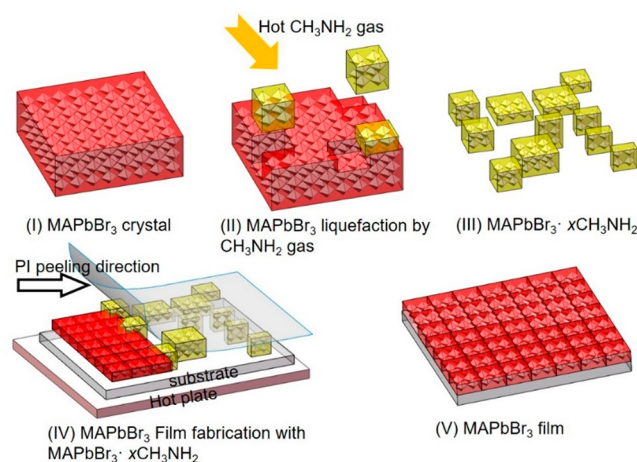
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room temperature, hot methylamine gas was introduced to liquefy the MAPbBr<sub>3</sub> crystals. By comprehensively understanding material and crystallization properties of the precursor in the hot methylamine gas environment, we achieved dense MAPbBr<sub>3</sub> films with crystallographically oriented grain arrangement that show single-crystal-like properties and contribute to the high responsivity and fast response speed in wide channel (100 μm) photodetectors. We further unveil a formation mechanism in which the continuous mosaic of MAPbBr<sub>3</sub> cuboids resulted from the large density of nuclei within the precursor and the suppression of convection-induced defects in the viscous precursor. We believe that this new route to assemble MAPbBr<sub>3</sub> cuboids into high-quality MAPbBr<sub>3</sub> films will further diversify the range of perovskite fabrication processes, thereby providing new strategies for perovskite research and device design.

The schematic diagrams for MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor preparation are shown in Scheme 1 (I–III), with the detailed

**Scheme 1. Schematic Diagrams for MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> Precursor Preparation and MAPbBr<sub>3</sub> Formation by Pressure-Assisted Soft-Cover Deposition<sup>a</sup>**



<sup>a</sup>(I) MAPbBr<sub>3</sub> crystal; (II) MAPbBr<sub>3</sub> single crystal liquefied by hot CH<sub>3</sub>NH<sub>2</sub> gas; (III) MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor; (IV) MAPbBr<sub>3</sub> film fabrication by pressure-assisted soft-cover deposition; (V) MAPbBr<sub>3</sub> film.

preparation described in the Experimental Methods section. Briefly, CH<sub>3</sub>NH<sub>2</sub> solution in water was added in a flask containing an excess amount of KOH and the mixture was heated at 70 °C in an oil bath. The produced hot CH<sub>3</sub>NH<sub>2</sub> was dried by CaO and then introduced into a vessel with MAPbBr<sub>3</sub> crystals to form MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> (the value of *x* will be discussed later). We studied the molecular interaction between CH<sub>3</sub>NH<sub>2</sub> and MAPbBr<sub>3</sub> by nuclear magnetic resonance (NMR), as shown in Figure S1. <sup>1</sup>H NMR peaks of the protons adjacent to nitrogen and carbon in CH<sub>3</sub>NH<sub>2</sub> were reported to be located at 1.15 and 2.26 ppm, respectively.<sup>30</sup> The <sup>1</sup>H NMR peaks of MABr (Figure S1a) at 7.54 and 2.35 ppm correspond to the resonances of protons from –NH<sub>3</sub><sup>+</sup> and –CH<sub>3</sub><sup>+</sup>, respectively. The peak located at 4.12 ppm for MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> (Figure S1b) is roughly halfway between 1.15 ppm of –NH<sub>2</sub> (CH<sub>3</sub>NH<sub>2</sub>) and 7.54 ppm of –NH<sub>3</sub><sup>+</sup> (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>). The peaks corresponding to the –CH<sub>3</sub> protons are slightly changed. These results suggest that MAPbBr<sub>3</sub> and CH<sub>3</sub>NH<sub>2</sub> mainly interact through the –NH<sub>3</sub><sup>+</sup> (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>) and –NH<sub>2</sub> (CH<sub>3</sub>NH<sub>2</sub>) groups.

We found that the precursor formed in Scheme 1 (III) turns into a solid when stored in a sealed vessel at room temperature for about 1 h and changes back to liquid phase when heated at a temperature of ~50 °C or higher, as shown in Figure 1a. This

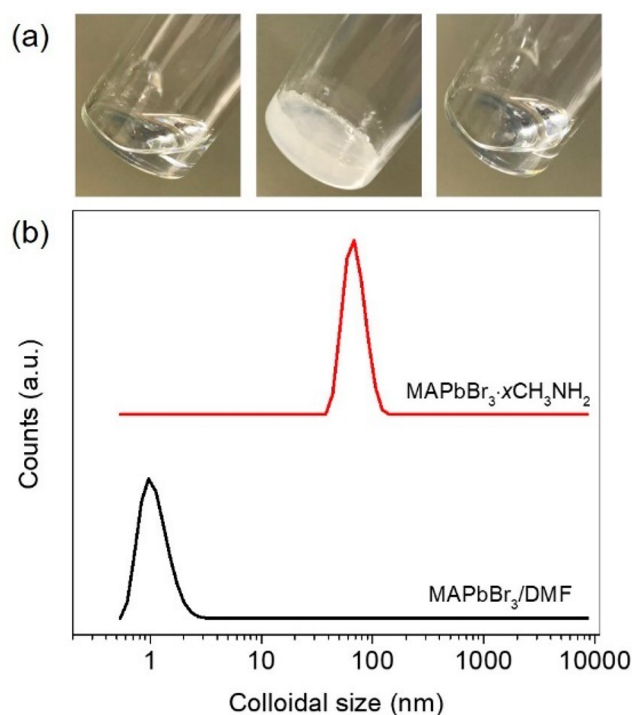


**Figure 1.** (a) Fresh MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor (left), stored at room temperature for 1 h (middle), and liquid MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor kept at 50 °C for 30 min (right). (b) DLS for MAPbBr<sub>3</sub>/DMF solution and MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor at ~50 °C.

phenomenon has not been reported previously for methylamine-based treatment.<sup>30–32</sup> We speculated that the solidification of MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> might be due to the stronger bonding of bromine anions to the neighboring cations and stronger Br···H–N hydrogen bonds, resulting from the larger electronegativity (2.96) and smaller Shannon ionic radius (1.96 Å) of bromine compared with those of iodine (2.66 and 2.2 Å for electronegativity and atom radius, respectively), which also make CH<sub>3</sub>NH<sub>2</sub> molecules more challenging to insert into the bromide perovskite than into the iodide analogue. This rationalizes the importance of using more thermally active hot CH<sub>3</sub>NH<sub>2</sub> gas to facilitate the reaction with MAPbBr<sub>3</sub>. Additionally, the solidification of MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor at room temperature necessitates the use of hot gas to maintain the flowing state of the precursor during preparation; if processed at room temperature, solid MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> may encase the unreacted MAPbBr<sub>3</sub> crystals and block further reaction, slowing the transition from pure perovskite to pure precursor. Overall, this first report of a solid CH<sub>3</sub>NH<sub>2</sub>-based precursor for MAPbBr<sub>3</sub> at room temperature offers the advantage of easy and safe transportation, facilitating the use of perovskite within practical applications.

The colloidal chemistry of liquid MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor (at 50 °C) was next studied by dynamic light scattering (DLS) and compared with a typical MAPbBr<sub>3</sub>/DMF precursor, as shown in Figure 1b. For MAPbBr<sub>3</sub>/DMF, the very small colloidal size (~1 nm average) reflects the good solvation of the polar solvent, in accordance with the literature.<sup>33</sup> The

MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor exhibits a much larger colloidal size (~74 nm average), which could facilitate in obtaining large grains in the perovskite film due to a prospective correlation between the film grain size and precursor colloidal size.<sup>34</sup> We converted the DLS peak representative of large colloids to that of small colloids (~1.3 nm) when MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> was added into DMF (Figure S2). This observation suggests that the large colloidal size in MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> stems from the absence of traditional polar solvents in the precursor. The coordination number of CH<sub>3</sub>NH<sub>2</sub> in MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor was determined by comparing the mass before and after liquefaction, that is, *x* ≈ 2.8, which is smaller compared to the value of 4 for MAPbI<sub>3</sub>, perhaps due to the lower activity of MAPbBr<sub>3</sub> with CH<sub>3</sub>NH<sub>2</sub>.

The viscosity of liquid MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor at 50 °C was also measured, yielding a value of ~1000 cP, which is significantly higher than typical polar-solvent-based precursors (with the largest reported value of <20 cP<sup>35</sup>). The high viscosity is rationalized by the lack of liquid polar solvent in the MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor. The MAPbBr<sub>3</sub> concentration of the precursor was calculated to be 3.94 M, i.e., rather high in comparison with the values (<2 M) of typical polar-solvent based precursors, due to the limited solubility offered by the solvents.<sup>36–41</sup> The high viscosity of the MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor is an important factor in suppressing convection-induced defects in scalable film fabrication processes.<sup>42</sup> Here, we fabricated MAPbBr<sub>3</sub> films by pressure-assisted soft-cover deposition using the viscous MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor at 50 °C (hereinafter abbreviated as “present route”). Schematic illustrations of pressure-assisted soft-cover deposition appear in Scheme 1 (IV and V), with details of the process described in the Experimental Methods section. The crystallization process during soft-cover deposition is very fast (~3 s), presumably because the gas component, CH<sub>3</sub>NH<sub>2</sub>, is very easily evacuated from the liquid precursor. We studied the morphology of the present MAPbBr<sub>3</sub> films by scanning electron microscope (SEM) imaging and compared them with typical spin-coated MAPbBr<sub>3</sub> films from MAPbBr<sub>3</sub>/DMF solution (hereinafter abbreviated as “control”), as shown in Figure 2. A top-view SEM image of the present route MAPbBr<sub>3</sub> film (Figure 2a) shows a continuous mosaic of regular MAPbBr<sub>3</sub> cuboids. The same compact films at a lower magnification can be found in Figure S3. A cross-sectional SEM image of the film (Figure 2b) shows well-aligned block-like MAPbBr<sub>3</sub> crystals, enabling the formation of a compact film with a columnar structure. No convection-induced defects (circular patterns<sup>42</sup>) nor large gaps between domains<sup>43</sup> appear in the present MAPbBr<sub>3</sub> film, as shown by the SEM image in Figure 2a,b. These results suggest the effectiveness of the viscous MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor in suppressing convection and thus its potential for application in scalable processes. The SEM images for the control (Figure 3c,d) show loosely distributed and often deformed MAPbBr<sub>3</sub> cuboids. Discontinuous MAPbBr<sub>3</sub> cuboids have been frequently reported,<sup>19,28,44</sup> suggesting general difficulty in controlling the continuity of MAPbBr<sub>3</sub> cuboid films using previously reported processes. In contrast, the continuity of MAPbBr<sub>3</sub> cuboids in this work benefits from the high concentration and viscosity of the MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor and the large density of nuclei, which ensure that cuboids connect during nuclei growth.<sup>21</sup> Further, the concentrated viscous MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor with easy-to-remove CH<sub>3</sub>NH<sub>2</sub> benefits from the fabrication of thick MAPbBr<sub>3</sub> films, a desirable form for X-ray

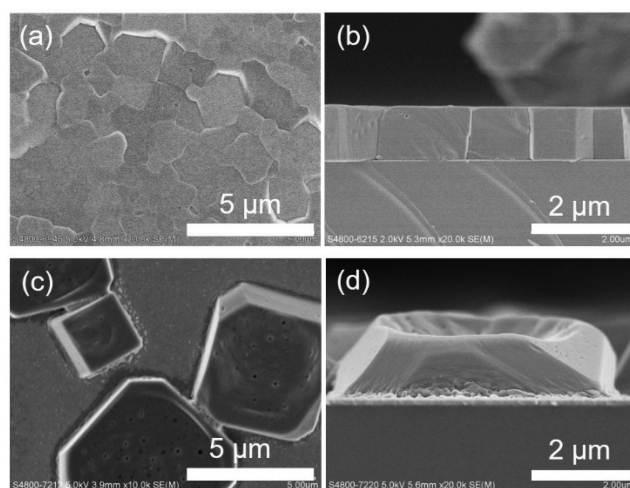


**Figure 2.** SEM images of MAPbBr<sub>3</sub> films. (a and b) Top-view and side-view SEM images, respectively, of MAPbBr<sub>3</sub> films prepared with MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor by pressure-assisted soft-cover deposition. (c and d) Top-view and side-view SEM images, respectively, corresponding to films prepared with a MAPbBr<sub>3</sub>/DMF precursor by spin-coating.

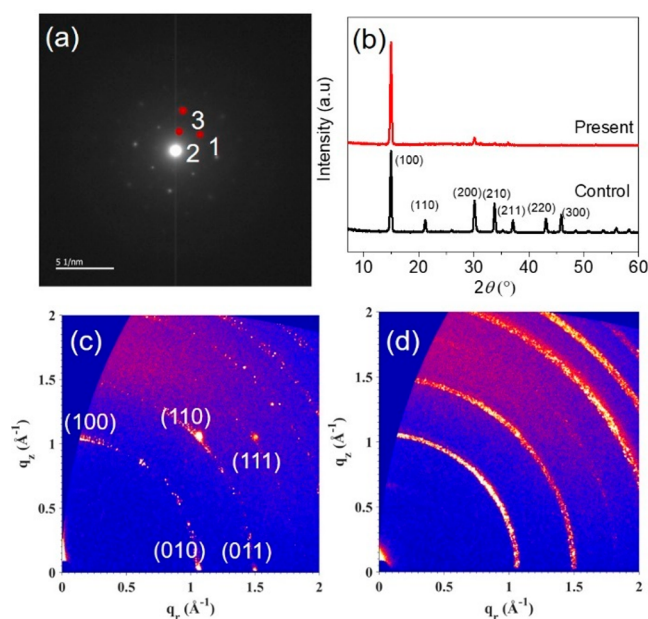


**Figure 3.** (a) SAD pattern of the present MAPbBr<sub>3</sub> film. (b) XRD patterns of the present MAPbBr<sub>3</sub> film and that for the control. (c and d) GIWAXS of the present MAPbBr<sub>3</sub> films and the control, respectively.

detection<sup>45,46</sup> and light management in solar cells, using a layer-by-layer approach (Figure S4).<sup>47–49</sup>

The distinct diffraction of the selected-area diffraction (SAD) pattern shown in Figure 3a suggests good crystallinity of the present MAPbBr<sub>3</sub> films. The SAD yields (110), (100), and (200) facets of the cubic MAPbBr<sub>3</sub> phase. As seen in the X-ray diffraction (XRD) pattern (Figure 3b), the control MAPbBr<sub>3</sub> films exhibit (100), (110), (200), (210), etc. peaks, while the present route mainly shows strong peaks for the (100) and (200) planes, suggesting an oriented arrangement of MAPbBr<sub>3</sub> crystals in the latter case. We further studied the crystal orientation by grazing-incidence wide-angle X-ray scattering (GIWAXS), as shown in Figure 3c,d. The discrete diffraction

spots of the present MAPbBr<sub>3</sub> film suggest an ordered crystal alignment, while the control shows isotropic diffraction rings resulting from randomly oriented crystals, in accordance with the XRD results in Figure 3b.

As the ultraviolet–visible (UV–vis) absorption and photoluminescence (PL) spectra show in Figure 4a, the MAPbBr<sub>3</sub> film

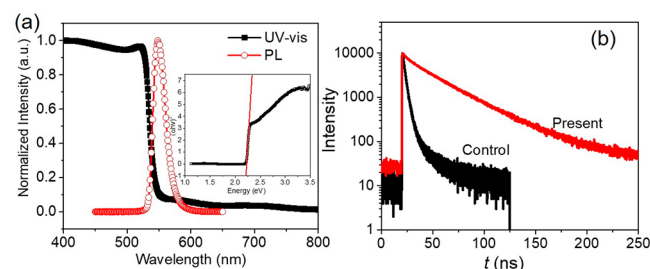


**Figure 4.** (a) UV–vis absorption spectrum and steady-state PL spectrum, excited by 375 nm pulse laser, of the present MAPbBr<sub>3</sub> film. The inset is the corresponding Tauc plot displaying the extrapolated optical band gap. (b) Time-resolved photoluminescence (TRPL) dynamics of the present MAPbBr<sub>3</sub> film and the control, excited by 375 nm pulse laser.

fabricated using the present route displays an optical absorption cutoff at ~547 nm, with the inset showing the corresponding Tauc plot and the extrapolated optical band gap of 2.24 eV, close to the value reported for bulk MAPbBr<sub>3</sub> single crystal or that of MAPbBr<sub>3</sub> ISC (2.18–2.24 eV, as listed in Table S1). Table S1 also indicates that the PL emission (560–574 nm) of normal single crystals and ISC MAPbBr<sub>3</sub> films tends to red shift compared with that of polycrystalline MAPbBr<sub>3</sub> (<545 nm) due to a combination of effects of photocarrier diffusion and reabsorption,<sup>50</sup> except for the very high-quality MAPbBr<sub>3</sub> single crystals by low-temperature-gradient crystallization (LTGC). The PL emission peak of the present MAPbBr<sub>3</sub> lies at 548 nm, in agreement with its optical band gap and close to the value of LTGC-MAPbBr<sub>3</sub>. The time-resolved photoluminescence (TRPL) dynamics of the present MAPbBr<sub>3</sub> film is shown in Figure 4b. The PL decay curve is well fitted by a biexponential decay model, yielding a fast time constant of  $6 \pm 2$  ns and a slow time constant of  $34 \pm 8$  ns. The fast time constant, presumably related to surface recombination, is comparable with the ISC MAPbBr<sub>3</sub> film ( $\sim 7$  ns<sup>28</sup>). The slow time constant, characterizing bulk recombination, is shorter than that of the ISC MAPbBr<sub>3</sub> film ( $\sim 189$  ns), while it is still much longer than that of polycrystalline MAPbBr<sub>3</sub> films, which exhibit a lifetime of only several nanoseconds (see Table S1 for comparison details). The control MAPbBr<sub>3</sub> film in this work also shows a very short average lifetime of  $\sim 5$  ns, corresponding to the reported time scale in Table S1. Because PL lifetime is related to recombination caused by defects, the longer PL lifetime suggests the good quality of the present MAPbBr<sub>3</sub> films. We studied the transport properties of the present MAPbBr<sub>3</sub> film using the Hall method. P-type conduction, a carrier density of  $1.7 \times 10^9$  cm<sup>-3</sup>, and a high carrier mobility value of 32 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> were obtained, comparable with the values for ISC MAPbBr<sub>3</sub> films and bulk single crystals (Table S1). The long time constant and large mobility of the present high-quality MAPbBr<sub>3</sub> film indicates single-crystal-like properties.

To prove the tight connection between MAPbBr<sub>3</sub> cuboids and the high-quality film, we fabricated large channel width (100  $\mu$ m between two adjacent electrodes) photodetectors and tested the

device performances. Photodetector current–voltage ( $J$ – $V$ ) curves were measured in the dark and under illumination ( $\lambda = 530$  nm), with light intensities ranging from 9.5 to 130.4  $\mu$ W cm<sup>-2</sup> (Figure S5). Responsivity ( $R$ ), the photocurrent generated per unit of incident light power), external quantum efficiency (EQE), and detectivity ( $D^*$ ) (shot-noise limited) were determined from the  $J$ – $V$  results under  $-5$  V bias, as shown in Figure 5a–c, respectively (calculation details appear in the

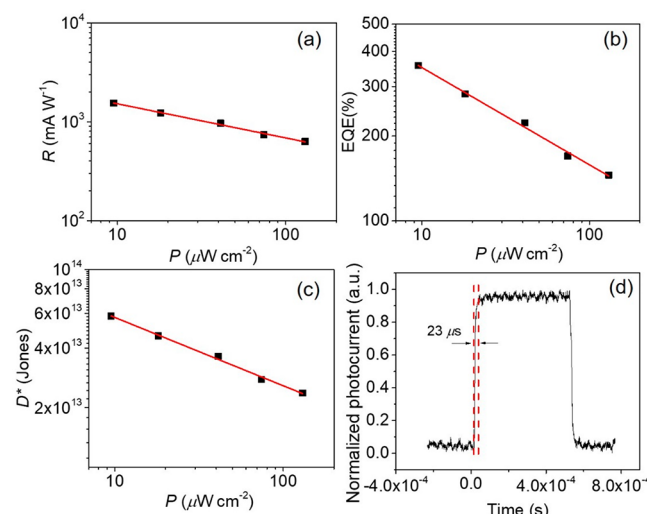


**Figure 5.** (a–c) Responsivity ( $R$ ), external quantum efficiency (EQE), and detectivity ( $D^*$ ), respectively, determined from the current–voltage results under  $-5$  V bias, which were measured in dark and under illumination using a 530 nm LED, with light intensities ranging from 9.5 to 130.4  $\mu$ W cm<sup>-2</sup> (see Figure S5). (d) Response time of the present MAPbBr<sub>3</sub> photodetectors under  $-5$  V bias.

**Supporting Information.**  $R$ , EQE, and  $D^*$  all decrease linearly with increasing light intensity, because more charge recombination is expected under higher light intensity, with values of approximately  $1.5 \times 10^3$  mA W<sup>-1</sup>, 356%, and  $5.8 \times 10^{13}$  Jones, respectively, under 9.5  $\mu$ W cm<sup>-2</sup> illumination. The high EQE > 100% means the photodetectors belong to a photoconductor type.<sup>51</sup> We summarize some of the typical device structures and photodetection parameters in Table S2. Due to the very different device structures, dimensions, and measurement parameters, such as light intensity and wavelength, comparing results across different studies is difficult. Nevertheless, Table S2 shows that the present MAPbBr<sub>3</sub> film has promising properties with respect to photodetection application, when considering both the photodetection ability and ease of fabrication. Further, a fast response time (the period when the photocurrent increases from 90% to 10% of the saturated value) of 23  $\mu$ s was obtained for the present MAPbBr<sub>3</sub> photodetector under  $-5$  V bias (Figure 5d). This value is shorter than those reported for ISC MAPbBr<sub>3</sub> films, bulk MAPbBr<sub>3</sub> single crystals, and MAPbBr<sub>3</sub> nanostructures (Table S2). We also fabricated bulk MAPbBr<sub>3</sub> single-crystal photodetectors with the same active channel width (100  $\mu$ m), which showed a rather long response time of 53  $\mu$ s (Figure S6), on the same time scale with the literature values (Table S2). The fast response confirms the high-quality crystals achieved with the new synthesis route for MAPbBr<sub>3</sub> films, since the response speed of a photodetector strongly correlates to charge transport and collection. Consequently, the above results confirm that the mosaic of MAPbBr<sub>3</sub> cuboids achieved with the present route are tightly connected and that the high quality of the present

MAPbBr<sub>3</sub> films contributes to a promising light response when applied in photodetectors.

## CONCLUSION

In conclusion, we have proposed and demonstrated a new method to fabricate MAPbBr<sub>3</sub> films based on a MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor prepared with hot methylamine gas coupled with a pressure-assisted soft-cover deposition approach. Features of the precursor and resulting MAPbBr<sub>3</sub> films have also been evaluated. The high quality of the MAPbBr<sub>3</sub> films, which consist of compactly arrayed and crystallographically aligned MAPbBr<sub>3</sub> cuboids, is resulted from the large density of the nuclei and high viscosity of the precursor, as well as the ease of removing CH<sub>3</sub>NH<sub>2</sub> during the soft-cover process. We have fabricated wide channel (100 μm) photodetectors with the dense MAPbBr<sub>3</sub> films and achieved promising responsivity and a very fast response speed of 23 μs, suggesting that the aligned cuboids are in good optoelectronic connection. This new route is expected to provide a complementary strategy for future perovskite fabrication and device design.

## EXPERIMENTAL METHODS

**MAPbBr<sub>3</sub> Single-Crystals Synthesis.** All materials were used as received unless otherwise stated. Lead bromide (PbBr<sub>2</sub>, 98%, TCI) and methylammonium bromide (CH<sub>3</sub>NH<sub>3</sub>Br, 98%, Dyesol) were mixed in dimethylformamide (DMF, 1 mL, Acros, extra dry) with a molar ratio of 1:1 to form a 1 M solution, which was stirred at room temperature for 6 h and filtered using a 220 nm PTFE filter. Small MAPbBr<sub>3</sub> seeds (~1 mm edge length) were added in the solution, and the solution was heated up to 80 °C in an oil bath and kept for 6–8 h for crystal growth. The formed MAPbBr<sub>3</sub> single crystals were then collected and dried at 60 °C under a vacuum for approximately 12 h.

**MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> Precursor Preparation and Film Fabrication.** KOH pellets (5 g) were put into a suction flask (250 mL), and then, 15 mL of methylamine solution (40 wt % in water, TCI) was added into the flask and constantly stirred at 150 rpm in an oil bath with a temperature of 70 °C. The generated CH<sub>3</sub>NH<sub>2</sub> gas then passed through a drying tower filled with desiccant (CaO) to remove moisture. The dried CH<sub>3</sub>NH<sub>2</sub> gas was constantly introduced into the bottle (without heating) containing bulky MAPbBr<sub>3</sub> single crystals to gradually form a colorless and transparent MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> liquid. The bottle reached a temperature of ~40 °C during the reaction between CH<sub>3</sub>NH<sub>2</sub> and MAPbBr<sub>3</sub>. To ensure sufficient interaction between the gas and the single crystals, the bottle was sealed with parafilm, and the formed liquid was collected over time with a pipet. The MAPbBr<sub>3</sub> film was prepared by pressure-assisted soft-cover deposition as reported with slight modification.<sup>31,32</sup> Briefly, 20 μL of preheated (~50 °C) perovskite precursor was dropped onto a 2 cm × 2 cm substrate, which was kept at ~50 °C, and then, a preheated (~50 °C) polyimide (PI) film (Dupont, KF5025L, thickness = 0.125 mm, RMS = 0.6 nm) was covered onto the precursor. A piece of preheated glass (~50 °C) was covered on the PI film and was pressed evenly to spread the liquid precursor onto the whole substrate. Then, the covered glass and PI film were removed at a rate of ~55 mm/s while heating (~50 °C), and the formed precursor film on the substrate was further heated at ~50 °C for 10 min to evaporate the CH<sub>3</sub>NH<sub>2</sub> gas and to fully form the MAPbBr<sub>3</sub> film. Besides the thinner films shown in Figure 2a,b, the thick MAPbBr<sub>3</sub> film prepared using the MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor (as shown in Figure S4) was prepared using two distinct MAPbBr<sub>3</sub> layers. Different from the pressure-assisted soft-cover deposition, it was fabricated with a nylon hairbrush with hair length ~1 cm on a 50 °C hot plate. The top layer was deposited (i.e., "painted") onto the bottom layer within ~20 s of the first layer, while being maintained at 50 °C. The film was held at 50 °C for 10 min to evaporate the excess CH<sub>3</sub>NH<sub>2</sub> and to form MAPbBr<sub>3</sub>.

**Material Characterizations.** <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) Fourier-transform NMR spectrometer.

The samples were dissolved in DMSO-*d*<sub>6</sub> and tested at 298 K. The DLS data were collected on a Malvern Zetasizer Nano ZS90 equipped with an internal HeNe laser (λ = 633.0 nm). The typical MAPbBr<sub>3</sub>/DMF solution had a concentration of 1 M, and the molar ratio of MABr and PbBr<sub>2</sub> was 1:1. DLS of the MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> precursor was measured at ~50 °C in a sealed quartz cuvette. The coordination number was calculated according to the molar ratio of absorbed CH<sub>3</sub>NH<sub>2</sub> to MAPbBr<sub>3</sub> crystals, which was obtained by weighing the mass of MAPbBr<sub>3</sub> crystals and the liquid that forms after reacting with CH<sub>3</sub>NH<sub>2</sub>. The MAPbBr<sub>3</sub> concentration was calculated according to the mass per volume, i.e., the mass of 200 μL of MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> was weighed to be 0.446 g. The viscosity of MAPbBr<sub>3</sub>·*x*CH<sub>3</sub>NH<sub>2</sub> was tested at ~50 °C under atmospheric pressure using an Ubbelohde viscometer with a capillary diameter of 1 mm. The time *t* of each precursor passing through the capillary was recorded, and the dynamic viscosity (cp) was calculated from the time *t* (s) and the density of precursor *ρ* (g cm<sup>-3</sup>) according to Poiseuille's law. The powder X-ray diffraction pattern (PXRD) was obtained using Cu Kα radiation with a λ of 1.54056 Å (Bruker D2 Phaser). The transmission electron microscopy (TEM) was tested with a FEI Tecnai G2 20. The morphology of the perovskite film was measured with SEM (Hitachi S-4800 FEG) using an accelerating voltage of 5 kV. GIXWAXS measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300 K detector. The incidence angle was 0.3°. The UV–vis absorption spectra were obtained from a home-built system with a xenon lamp as the light source and an integrating sphere associated with a charge-coupled device (CCD, Ocean Optics QE Pro) as the detector. The PL spectra were measured with a 375 nm picosecond pulse laser (PicoQuant LDH-P-C-375) and a photomultiplier (PMA-C 192-M) detector. Hall effect was measured in the dark using a physical property measurement system (PPMS, Quantum Design) with magnetic field intensity of 0.6 T and temperature of 300 K. The sample (~1.5 μm in thickness) for Hall measurement was fabricated on a piece of glass with a dimension of 1.7 cm × 1.7 cm, with four square Au/Cr metal electrodes (thickness: 50 nm/8 nm; area ~9 mm<sup>2</sup>) evaporated on the four corners.

**Device Fabrication and Characterizations.** Cr (10 nm)/Au(30 nm) electrodes were evaporated on the MAPbBr<sub>3</sub> film at a pressure ca. 5 × 10<sup>-6</sup> Torr to make the photodetector structure. The dimension of the MAPbBr<sub>3</sub> active channel between two adjacent Cr/Au pads was 100 μm in width, 4 mm in length, and 1.5 μm in thickness. The active area of the device was about 0.4 mm<sup>2</sup>. Current–voltage (*I*–*V*) curves of the photodetectors were measured using a Keithley 2635 SourceMeter in the dark and under illumination using 530 nm wavelength light with intensity values of 9.5, 18.1, 41.1, 74.2, and 130.4 μW cm<sup>-2</sup>. The response time of the photodetector was measured under –5 V bias with 490 nm light.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c04516>.

Figures of NMR spectra, DLS results, SEM images, current–voltage curves, and response time, tables of optical band gap, optical absorption cutoff, PL emission peak, PL lifetime, and mobility and device parameters, and discussions of calculations (PDF)

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## Notes

The authors declare no competing financial interest.

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