Scalable Route to the Fabrication of CH3NH3PbI3 Perovskite Thin Films by Electrodeposition and Vapor Conversion

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ABSTRACT: Hybrid halide perovskite thin films are applicable in a wide range of devices such as light-emitting diodes, solar cells, and photodetectors. The optoelectronic properties of perovskites together with their simple and inexpensive film deposition methods make these materials a viable alternative to established materials in these devices. However, the potential of perovskite materials is compromised by the limitations of the existing deposition methods, which suffer from trade-off among suitability for large-scale industrial production in a batch or roll-to-roll manner, deposition area, film quality, and costs. We addressed these limitations by developing a deposition method that is inexpensive, applicable to large substrate areas, scalable, and yields high-quality perovskite films. In this study, the low-cost electrodeposition (ED) method and sequential exposure to reagent vapors produce CH$_3$NH$_3$PbI$_3$ perovskite films with thickness nonuniformity below 9% on a centimeter scale. PbO$_2$ films are electrodeposited first and then undergo two vapor conversion steps, with HI vapor in the first step and CH$_3$NH$_3$I vapor in the second step. The second step yields CH$_3$NH$_3$PbI$_3$ films that are continuous and consist of micrometer-sized grains. This process allows the preparation of both α- and β-phase CH$_3$NH$_3$PbI$_3$ films, offers a simple means to control the film thickness, and works over a wide range of film thicknesses. In this work, films with thicknesses ranging from 100 nm to 10 μm were prepared. ED and vapor conversion are inherently scalable techniques and hence the process described herein could benefit application areas in which large device areas and throughput are required, such as the production of solar cells.

INTRODUCTION

Hybrid halide perovskites (hereafter perovskites), such as CH$_3$NH$_3$PbI$_3$ (hereafter MAPbI$_3$), are a recently emerged class of materials that can be employed in light-emitting diodes (LEDs), thin-film transistors (TFTs), optically pumped lasers, photodetectors, resistive switching random access memory (ReRAM), and solar water splitting; however, they are perhaps the most known for enabling high-efficiency perovskite solar cells. Perovskite devices with diverse architectures composed of planar thin films are some of the major requirements for improving device performance. The most common approach for depositing perovskites is spin coating. Spin-coating approaches can be further divided into those relying on single-step, two-step, and solvent-engineering methods. All of these methods are capable of producing perovskite films of sufficient quality. However, in spin coating, the film quality deteriorates with increasing deposition area. For that reason, devices prepared using spin-coating-based approaches typically have areas of a couple of square centimeters or less. Devices with larger areas therefore require alternative perovskite deposition methods, which are scalable.

Several scalable deposition methods that do not involve spin coating are applicable for perovskites. These methods rely on physical vapor deposition (PVD), chemical vapor deposition (CVD), atomic layer deposition (ALD), electro-deposition (ED) combined with conversion in solution, spray deposition (SD), and the doctor blade (DB) technique.

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Methods employing solutions, such as ED, SD, and DB, yield less-uniform films with a higher grain boundary density, whereas uniform perovskite films, typically with a low grain boundary density, are produced by vacuum techniques, such as PVD, CVD, and ALD. Because vacuum techniques are more expensive than solution-based methods, the existing scalable approaches for perovskite film deposition offer trade-offs between quality and cost.

Herein, we attempted to preserve the advantages of both quality and low-cost by first converting electrodeposited PbO$_2$ films into PbI$_2$ films with HI vapor and subsequently converting PbI$_2$ films into MAPbI$_3$ films with CH$_3$NH$_3$I vapor. We further explore the features of this deposition approach and film properties, such as thickness controllability and uniformity, that are important in a variety of perovskite film application areas. ED is a simple and inexpensive method that is applicable for the deposition of uniform coatings on substrates with areas on the order of square meters and with complex shapes. Therefore, ED of PbO$_2$ fulfills the low-cost and scale-up requirements. On the other hand, conversion of PbI$_2$ or postdeposition processing of MAPbI$_3$ with CH$_3$NH$_3$I vapor yields uniform perovskite films with a low grain boundary density, concurrently maintaining a reasonable processing cost. Furthermore, to the best of our knowledge, this work is the first to describe the conversion of a PbO$_2$ film into a PbI$_2$ film by HI vapor as well as the reactor design necessary for such a conversion. PbI$_2$ film fabrication methods are important because PbI$_2$ films serve as precursors for several halide perovskites, such as HC(NH$_2$)$_2$PbI$_3$ (FAPbI$_3$) and others.

**RESULTS AND DISCUSSION**

**Film Uniformity.** In perovskite solar cells, deviations from the optimal perovskite film thickness can decrease the performance either by reducing absorption or by extending the path the charge carriers need to traverse before collection. In the literature, perovskite thickness uniformity is typically assessed from SEM images of film cross sections recorded on a scale of a few micrometers. However, Liu et al. highlighted the disadvantages of this approach, demonstrating that spin-coated MAPbI$_3$ films that are uniform on a scale of a few micrometers reveal thickness variations of ±100% from the mean thickness on a larger scale. Herein, the thickness uniformity of the films was evaluated by thickness measurements at five distinct points across every film. Four measurement points were located at an equal distance from the two nearest deposition area borders, whereas the fifth one was located in the middle of the deposition area (Figure 1a).

**ED of PbO$_2$ Films.** Anodic ED of PbO$_2$ proceeds according to reaction 1.

\[
Pb^{2+}(aq) + 2H_2O(l) \rightarrow PbO_2(s) + 4H^+(aq) + 2e^- \tag{1}
\]

The color of the electrodeposited PbO$_2$ changed from beige to dark red with increasing film thickness. The film thickness becomes less uniform with increasing current density (Figure 1b). Increased current density causes the reactants to deplete in the vicinity of the substrate, allowing variations in the diffusion fluxes between the substrate edges and its center area to affect the uniformity of the coating. In the case of PbO$_2$ deposition, an excessively low current density leads to an impractically low growth rate. A sufficient growth rate and very uniform PbO$_2$...
Films are obtained at 0.25 mA cm\(^{-2}\). In addition, at 0.25 mA cm\(^{-2}\), the current distribution and film uniformity are governed by the geometry of the bath. Rotating the substrate by 45° with respect to its normal face-to-face orientation with the counter electrode alters the thickness profile of the deposited film and produces thinner PbO\(_2\) film in the area further from the counter electrode (Table 1, compare films A and B, see also Figure S1). Such a behavior suggests that proper optimization of the bath geometry can further improve the film uniformity. Uniformity of the PbO\(_2\) film is important because it is retained through the vapor conversion steps into the final MAPbI\(_3\) film.

All PbO\(_2\) films consist of grains of size 26 ± 11 nm (Figure 2a), which form larger agglomerates (Figure 2e). These agglomerates expand as the deposition proceeds and merge to form dense films (Figure 2b,c) with uniform coverage. The roughness of the films is affected by the size and shape of the agglomerates, for example, the root-mean-square (rms) roughness of a PbO\(_2\) film deposited for 725 s is 33 nm, which is 18% of the film thickness. Macroscopically, full coverage is displayed by all of the PbO\(_2\) films (Figure 2d,f). However, only the films deposited for 500 s or longer exhibit full coverage on a microscopic scale (Figure 2c), whereas in the films deposited for shorter periods, areas with an exposed FTO surface are observed (Figure 2e). Despite this lack of full coverage in thinner films, the amount of PbO\(_2\) deposited depends linearly on the deposition time, and the growth rate is 0.25 ± 0.01 nm s\(^{-1}\) (Figure 1c). In contrast, there is no correlation between deposition time and thickness nonuniformity. The thickness nonuniformity in the films is ≤9%.

The as-deposited PbO\(_2\) films contain a mixture of orthorhombic \(\alpha\)-PbO\(_2\) and tetragonal \(\beta\)-PbO\(_2\) phases (Figure 1d). The ratio of these phases was impossible to determine due to the broadness of the X-ray diffraction (XRD) reflections. Therefore, the mean density (9.71 g cm\(^{-3}\)) of the \(\alpha\) and \(\beta\) phases (9.87 and 9.55 g cm\(^{-3}\), respectively) was used for the thickness calculations. XRD reflections appear to broaden due to the small size of the grains, as observed with AFM and FESEM. According to the X-ray diffractograms measured with the \(\theta-2\theta\) geometry, these grains do not exhibit a preferential orientation.

### Table 1. Thicknesses of Electrodeposited PbO\(_2\) Films

| measured from | thickness (nm) | acetate bath (this work) | nitrate bath \(^{32}\) |
|---------------|---------|----------------|----------------|
| P1            | 53      | 58              | 98             | 109           |
| P2            | 53      | 51              | 101            | 108           |
| P3            | 47      | 42              | 88             | 79            |
| P4            | 46      | 43              | 89             | 85            |
| P5            | 46      | 40              | 92             | 83            |
| mean          | 49      | 47              | 94             | 93            |
| \(\sigma_{\text{rel}}\) | 7%      | 16%             | 6%             | 16%           |

Films A and B deposited at 0.25 mA cm\(^{-2}\) for 200 s. Film A deposited with the substrate surface parallel and B, with the substrate surface at 45° with respect to the counter electrode surface. P1 and P4 of film B were located on the substrate edge closest to the counter electrode. C was deposited at 0.25 mA cm\(^{-2}\) for 375 s, whereas D was deposited at 1.8 V for 30 s. Both C and D were deposited with the substrate surface parallel to the counter electrode surface. A–C were deposited in a 0.1 M Pb(CH\(_3\)COO)\(_2\), 1.0 M Na(CH\(_3\)COO) bath, whereas D was deposited in a 0.1 M Pb(CH\(_3\)COO)\(_2\), 0.2 M NaNO\(_3\), 0.1 M HNO\(_3\) bath. \(^{32}\) Figures illustrating the thickness profiles of the films and bath geometries are available in the Supporting Information (Figures S1 and S2). Positions of measurement points P1–5 are shown in Figure 1a.

**Figure 2.** (a) Atomic force microscopy (AFM) image, (b) cross-sectional and (c) top-view field emission scanning electron microscopy (FESEM) images, and (d) a photograph of a PbO\(_2\) film deposited at 0.25 mA cm\(^{-2}\) for 725 s. (e) FESEM image and (f) a photograph of a PbO\(_2\) film deposited at 0.25 mA cm\(^{-2}\) for 400 s. The outlined area in (e) is the exposed FTO surface.
PbO₂ films display an optical band gap of 1.4 ± 0.1 eV. This value is in agreement with the values reported previously for PbO₂. The EDX spectra revealed no impurities, and all of the films passed the Scotch tape adhesion test without delaminating. No delamination occurred even in the case of films grown for 5100 s, whose thickness, estimated from the growth rate (Figure 1c), is 1.3 μm.

In the literature, perovskite films have been made starting from electrodeposited lead monoxide (PbO) that is converted to PbI₂ or directly to MAPbI₃. However, ED of PbO requires unstable H₂O₂-containing solutions or additionally dimethyl sulfoxide, elevated temperature, and solution degassing to remove dissolved O₂. In contrast, PbO₂ ED does not require solution degassing and proceeds under ambient conditions in a stable aqueous solution. The acetate-based ED solution employed in this study results in a lower growth rate than that of the nitrate-containing solution used by Chen et al. On the other hand, the acetate solution produces more uniform films (compare films C and D in Table 1, see also Figure S2), and the lower growth rate enables more precise thickness control. Further comparison of ED-based processes for MAPbI₃ films is provided in Table S1.

Conversion of PbO₂ Films into PbI₂. The electrodeposited PbO₂ films were converted into PbI₂ films by exposing them to an excess of HI vapor, which, to the best of our knowledge, has not been reported elsewhere. The conversion occurs only at an elevated temperature; therefore, removing the reactor from the heat source too early will quench the conversion process and produce partially converted films. The iodine content of a set of partially converted PbO₂ films (Figure S3) and their phase compositions (Figure S4) suggest that for PbO₂ films deposited for 725 s or less, the conversion is completed in 90 min. The use of a glass reactor (Figure 3a) also allows us to visually observe the progress of the conversion (see Video S1). The appearance of the film changes during the conversion, due to changes in the band gap and roughness, which translate into changes in the reflectance and transmittance (see Figure S5 for UV–vis transmittance of as-deposited, partially converted, and fully converted films). Therefore, an indication of the completion of the conversion can be obtained from the lack of further changes in the color of the film. During the conversion, the reaction front advances from the edges of the PbO₂ film toward its center. The reaction appears to involve PbO₂ reduction by iodide (eq 2). The XRD patterns of the partially converted films (Figure S4) additionally suggest that this reaction may proceed through the PbI(OH) intermediate (eqs 3 and 4).

\[ \text{PbO}_2(s) + 4\text{HI}(g) \rightarrow \text{PbI}_2(s) + \text{I}_2(g) + 2\text{H}_2\text{O}(g) \]  

Figure 3. (a) Photograph and schematic picture of the reactor assembly for converting PbO₂ films into PbI₂ films. (b) X-ray diffractograms of PbI₂ films obtained by the conversion of PbO₂ films deposited for different times. The topmost diffractogram denoted by an asterisk was measured with the θ–2θ geometry, whereas other diffractograms were measured with a grazing incidence geometry. (c) PbI₂ film thickness as a function of the PbO₂ deposition time and PbO₂ film thickness. R² is 0.996 for the fitted curve on the left-hand-side graph and 0.995 for the one on the right-hand-side graph.
Furthermore, PbI₂ film thickness plotted against PbO₂ film deposition time reveals that the effective growth rate of PbI₂ films is 0.78 ± 0.02 nm/s. PbI₂ films demonstrate relative thickness variations of ±8% across the film. This value is correlated with the thickness variations in PbO₂ films, implying that the thickness profile (see films A and C from Table 1 and Figures S1 and S2) is retained on conversion. Examination of the PbI₂ film morphology reveals that during the conversion the grains also show slight lateral growth. The lateral growth explains the pinhole sealing in the PbI₂ films converted from the PbO₂ films deposited for 400 s (compare Figures 2e and 4a). The lateral growth is favorable because it compensates for the defects in the PbO₂ films and promotes the formation of dense PbI₂ films (Figure 4c). Pinholes still occur in PbI₂ films converted from PbO₂ films deposited for ≤200 s. All PbI₂ films appear macroscopically uniform (Figure 4d), whereas on a smaller scale, they consist of grains with different sizes (Figure 4a,b). The grain size seems to increase with increasing film thickness. For example, in the PbI₂ films converted from PbO₂ deposited for 725 s, the grain size is 0.33 ± 0.13 μm. This grain size is about 10 times larger than that of the original PbO₂ film and can be correlated to the more than doubled roughness (rms 79 nm) of the converted film. The roughness is, however, 14% of the PbI₂ film thickness, suggesting in relative terms that the surface has leveled a bit. PbI₂ films are yellow, translucent, and display an optical band gap of 2.4 ± 0.1 eV, which agrees with the value previously reported for PbI₂.48

Conversion of PbI₂ Films into CH₃NH₃PbI₃. The PbI₂ films made by conversion of electrodeposited PbO₂ films were finally converted into MAPbI₃ films by exposing them to CH₃NH₃I vapor. Conversion to MAPbI₃ proceeds in a reactor analogous to the reactor used for the conversion of PbO₂ to PbI₂ (see Figure S8). Conversion in an inert atmosphere (N₂ or Ar) leads to film deterioration, whereas conversion in static vacuum yields MAPbI₃ films (see Video S2) as desired. According to EDX, the films contain lead and iodine in amounts in agreement with the stoichiometry of MAPbI₃ (Figure 5a). Furthermore, the EDX spectra of the films contain nitrogen and carbon signals, but the limitations of EDX do not allow quantification of these light elements. No impurity elements were observed in the EDX spectra, and no PbI₂ reflections are observed in the XRD patterns of the films (see Figure S6 for comparison of the film diffractograms at different steps). If the conversion process is interrupted too early, PbI₂ reflections are still observed in the X-ray diffractograms of the partially converted films (Figure S9). The iodine content in the films increases linearly with time during the conversion to a level corresponding to that of MAPbI₃ (Figure S10) and remains constant thereafter. Because the thicknesses of the PbI₂ films are known, extrapolating the iodine content increase to a constant level and assuming that this increase is proportional to the conversion rate allows us to estimate the latter. The conversion rate determined with these assumptions is ca. 1.1 μmol of the PbI₂ film thickness per hour. The completion of the conversion of PbI₂ to MAPbI₃ can also be detected by the absence of further changes in the appearance of the film. These changes in the appearance are due to changes in the optical properties such as transmittance (Figure S11) of the film. Recently, Brenner et al. suggested that at elevated temperature the reaction of PbI₂ with CH₃NH₃I and the formation of MAPbI₃ proceed by a deconstruction–reconstruction mechanism.59

| PbO₂ film | deposition time (s) | thickness (nm) | hydroiodic acid (μL) | 50 mL reactor | 100 mL reactor |
|-----------|---------------------|----------------|----------------------|---------------|---------------|
|           | 100                 | 28 ± 2         |                      | 20            | 30            |
|           | 200                 | 54 ± 8         |                      | 20            | 30            |
|           | 300                 | 78 ± 8         |                      | 20            | 30            |
|           | 400                 | 103 ± 10       |                      | 40            | 40            |
|           | 500                 | 124 ± 7        |                      | 60            | 60            |
|           | 725                 | 180 ± 12       |                      | 60            | 80            |
|           | 1000                | 1275±          |                      | 300           |               |

*Thickness estimated from the growth rate (Figure 1c); the thickest film was converted to PbI₂ in 4 h.*

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PbO₂(s) + 3HI(g) → PbI(OH)(s) + I₂(g) + H₂O(g)  (3)

PbI(OH)(s) + HI(g) → PbI₂(s) + H₂O(g)  (4)

Pb⁴⁺ in PbO₂ is a hard Lewis acid and is easily reduced because the inert pair effect makes the lead +II oxidation state more stable than the +IV oxidation state. Iodide, a soft Lewis base, in accordance with the Lewis hard–soft acid–base principle, binds preferably to Pb(II), which is a soft Lewis acid.

Initial conversion experiments without silica gel revealed that the formed PbI₂ film is sensitive to humidity during conversion. As the conversion proceeds, water droplets may condense on the reactor walls and substrate. These droplets, upon contact, degrade the formed PbI₂ film versus PbO₂ (Figure 3b). Similar orientation is observed in PbI₂ films made in spin-coated PbI₂.32 PbI₂ has a two-dimensional surface in spin-coated PbI₂. However, (001) planes are predominantly parallel to the surface (see Figure S7). Consequently, the interlayer gaps extend through the PbI₂ films primarily with the (110) planes parallel to the surface (Figure 3b). This orientation is observed in PbI₂ films made by converting electrodeposited PbO₂ films in solution; however, (001) planes are predominantly parallel to the film surface in spin-coated PbI₂.32 PbI₂ has a two-dimensional layered structure, in which bonding between the layers is only due to weak interactions. These layers and interlayer gaps lie perpendicular to the film surface when (110) planes are parallel to the surface (see Figure S7). Consequently, the interlayer gaps extend through the film thickness, and in the subsequent conversion step to the perovskite, they may act as transport paths for the conversion reagent molecules.

PbI₂ is less dense (ρ = 6.10 g cm⁻³) than PbO₂ (ρ = 9.6–9.9 g cm⁻³); therefore, upon conversion, the volume of the PbO₂ grains should expand. In theory, if the grains would expand only perpendicular to the film surface, the film thickness (d) would increase by a factor of 3 (eq 5).

\[ d_{\text{PbI}_2} = \rho_{\text{PbO}_2} M_{\text{PbO}_2} / \rho_{\text{PbI}_2} M_{\text{PbI}_2} d_{\text{PbO}_2} = 3.07 d_{\text{PbO}_2} \]  (5)

A similar factor of 3.20 ± 0.10 is obtained experimentally from the PbI₂ versus PbO₂ film thickness plot (Figure 3c).
Controlling the duration of the conversion allows the preparation of different crystal phases of MAPbI₃. MAPbI₃ films crystallize in the tetragonal β-phase (Figure 5b), whereas the layer underneath is MAPbI₃. The α-phase at an elevated temperature. Therefore, prolonged annealing of the conversion process is complete induces the β ‒ α transition, and rapid removal of the reactor from the heat source prevents the reverse transition and yields α-phase films. The α-phase is less distorted from the ideal perovskite structure and is more compact compared with the β-phase. Such compactness can be beneficial to the stability of the perovskite. For instance, in the case of MAPbI₃−xBrₓ solid solutions, phase transition to the pseudocubic phase decreased the moisture sensitivity of the perovskite. For MAPbI₃ perovskite, Milot et al. reported that upon temperature increase and phase transition to the pseudocubic phase the rate constant for Auger recombination decreases. The Auger recombination rate is an essential parameter for devices with large effective carrier densities, such as lasers and concentrated photovoltaics. Furthermore, photovoltaic devices with pseudocubic MAPbI₃ exhibit less hysteretic behavior, in contrast to devices with the tetragonal phase. For films of either of the phases, XRD measurements with the 0 – 2θ geometry revealed no significant preferential orientation.

There appears to be no limit to the maximum convertible PbI₂ thickness. Even 10 μm thick MAPbI₃ films (Figure 6a) could be produced provided that the duration of conversion was long enough (24 h). One conversion of such thick film was interrupted at 2 h, and the cross section of this film revealed two distinct layers (Figure 6b). The contrast difference suggests that the topmost layer is MAPbI₃, whereas the layer underneath is unconverted PbI₂. The presence of PbI₂ is also indicated by PbI₂ reflections in the X-ray diffractogram of this film. The interrupted conversion allows us to evaluate the conversion rate by measuring the geometric thicknesses of the PbI₂ and MAPbI₃ layers from the film cross section. The rate is ca. 1.1 μm/h with respect to the thickness of the converted PbI₂ or 2 μm/h with respect to the thickness of the formed MAPbI₃ film, in agreement with the rate determined from the change in the iodine content in the films.

MAPbI₃ films should be thicker than the PbI₂ and PbO₂ films from which they were prepared because the MAPbI₃ phases are less dense (ρβ = 4.09 and ρα = 4.16 g cm⁻³) than PbI₂ or PbO₂. The thickness increase factor for the β-MAPbI₃ films obtained by an approach similar to the one in eq 1 is 1.97 with respect to that of PbI₂ and 6.06 with respect to that of PbO₂. The experimental factors, that is, 1.84 ± 0.04 with respect to that of PbI₂ (Figure 5c) and 5.84 ± 0.09 with respect to that of PbO₂, agree with the predicted thickness increase. The MAPbI₃ film thickness exhibits a linear dependence on the deposition time of the original PbO₂ film (Figure 5c) and the MAPbI₃ growth rate with respect to the PbO₂ deposition time is 1.42 ± 0.03 nm/s. The linear dependence implies that the MAPbI₃ film thickness can be conveniently and accurately controlled by the PbO₂ ED time. The deposition time and thus the MAPbI₃ thickness have no effect on the uniformity. The relative thickness nonuniformity of the MAPbI₃ films is 8.5%, a value markedly similar to the nonuniformities of the PbI₂ and PbO₂ films. The similarity suggests that MAPbI₃ inherits its thickness profile from the initial PbO₂ film, and this in turn explicitly demonstrates the significance of the PbO₂ uniformity. As discussed previously, the PbO₂ film uniformity could be improved by optimizing the ED bath geometry or alternatively by employing suitable bath additives.

MAPbI₃ films are black in color with metal-like reflective surfaces (Figure 7a,b). The surface roughness of the β-phase
films originating from the PbO$_2$ films deposited for 725 s is 78 nm (rms), and these films consist of grains of size 0.30 ± 0.12 μm. This grain size is similar to that of the preceding PbI$_2$ film converted from the PbO$_2$ film deposited for 725 s. In contrast to the β-phase films, the α-phase films originating from the PbO$_2$ films deposited for 725 s are smoother, with a surface roughness of 69 nm (rms), and consist of larger grains (size 0.55 ± 0.12 μm). A larger grain size is beneficial for the efficiency of perovskite-based devices, such as LEDs, TFTs, ReRAMs, and photovoltaic devices, as it translates to a lower grain boundary density, improving the charge transfer properties. Additionally, a lower grain boundary density should retard hydration and decomposition of the perovskite because grain boundaries facilitate transport of water molecules within the perovskite. The conversion of PbI$_2$ to MAPbI$_3$ leveled the films, similar to the conversion of PbO$_2$ to PbI$_2$; for instance, the rms roughness is 7% of the film thickness for the β-MAPbI$_3$ film originating from the PbO$_2$ film deposited for 725 s and 6% for the α-MAPbI$_3$ film originating from a similar PbO$_2$ film.

Markedly, the voids have been sealed even in the thinnest MAPbI$_3$ films originating from PbO$_2$ films deposited for 100 s (Figure 7d). The tendency for such self-sealing is an advantage of the vapor conversion method, as it allows some imperfections in the intermediate PbI$_2$ and PbO$_2$ films without compromising the capability to produce continuous MAPbI$_3$ films, at least in the examined thickness range (0.1–10 μm).

According to UV−vis measurements, both α- and β-MAPbI$_3$ films exhibit an optical band gap of 1.6 ± 0.1 eV. These values agree with the values previously reported for these MAPbI$_3$ phases. Furthermore, MAPbI$_3$ films behave as photoconductors according to I−V measurements (Figure S12). A potential difference of 0.9 V was measured between the FTO...
bottom contact and the In–Ga eutectic top contact of the 1.1 μm β-MAPbI3 film when it was illuminated with 1000 W m⁻² as opposed to zero potential difference measured without illumination. These observations indicate that the MAPbI₃ films made by vapor conversion of electrodeposited PbO₂ are photoactive.

Our preliminary results indicate that PbI₂ films react also with HC(NH₂)₂I (formamidinium iodide (FAI)) under the same conditions as their reaction with CH₃NH₃I. However, the conversion process is much slower with FAI, and even after 24 h, a minor reflection at 12.4°, indicative of unreacted PbI₂, is observed in the X-ray diffractogram of the film (Figure S13).

### **CONCLUSIONS**

Uniform MAPbI₃ films are reproducibly prepared by ED together with a two-step vapor conversion. Grain growth during the vapor conversion steps mitigates microscopic voids in the films to some extent, improving the quality of the final MAPbI₃ film. The crystal phase of the MAPbI₃ film as well as its grain size can be adjusted by changing the duration of the second vapor conversion step, whereas adjusting the ED duration allows simple control over the film thickness. A wide range of MAPbI₃ film thicknesses, from tens of nanometers to tens of micrometers, is accessible with the described approach. ED lacks an inherent substrate size limit and is scalable in a roll-to-roll or brush manner or to large batches, whereas vapor exposure steps are in principle limited only by the reaction vessel size. Together, the qualities of this approach make it a promising deposition method for a wide range of perovskite film applications, such as LEDs, TFTs, ReRAM, photodetectors, and photovoltaics. Future work may focus on further upscaling of the method. Alternatively, further simplification of the PbO₂ to PbI₂ conversion step by exploiting gaseous hydrogen iodide may be explored.

### **MATERIALS AND METHODS**

**Substrate Preparation.** TEC 7 fluorine-doped tin dioxide-coated glass substrates (FTO) were obtained from SOLEMS. Before ED, the substrates were rinsed with ethanol, dried with compressed air, and annealed in an air oven at 350 °C for 2 h. The heating rate was 3 °C/min.

**ED of PbO₂ Films.** An aqueous solution containing 0.10 M lead(II) acetate trihydrate (Sigma-Aldrich, 99%) and 1.00 M sodium acetate (Sigma-Aldrich, 99%) served as an ED bath for PbO₂ films. The solution was prepared by first dissolving sodium acetate, followed by initial pH adjustment to 5.6–5.8. Next, lead(II) acetate trihydrate was dissolved, followed by final pH adjustment to 5.5. The pH adjustments were done with 5 M acetic acid and 3 M sodium hydroxide. The solutions were prepared using 18 MΩ cm resistivity water from a Millipore Milli-Q system.

ED was performed without stirring at ambient temperature with an Autolab PGSTAT20 potentiostat–galvanostat and a three-electrode arrangement. FTO slides (5.0 × 2.5 cm²) acted as working electrodes, with the active deposition area being 10 cm² (4.0 × 2.5 cm²). A cylinder-shaped platinum net (r = 1.5 cm, h = 3.7 cm) was used as the counter electrode and an Ag/AgCl/KCl (3 M) electrode as the reference electrode. EDs were done galvanostatically at a current density of 0.25 mA cm⁻² unless specified otherwise.

**Conversion of PbO₂ to PbI₂.** Conversion of the as-deposited PbO₂ to PbI₂ was carried out in a 100 mL Erlenmeyer flask with a ground-glass joint (VWR; 29/32). Hydroiodic acid (20–300 μL, 55%, no stabilizer; Sigma-
Aldrich) was pipetted into a glass boat \((l = 5 \text{ cm}, w = 1 \text{ cm})\), and the boat was transferred into the flask. A total of 250 mg of silica gel granules \((2−6 \text{ mm}; \text{VWR Chemicals})\) was spread around the boat inside the flask to absorb excess water from the hydroiodic acid. A substrate holder was bent from a titanium foil (Alfa Aesar, 0.25 mm, 99.5%) and placed over the boat. The PbO\(_2\) films were placed onto the holder facing upward. The flask was then flushed with nitrogen (99.999%) for 2 min and sealed with a glass stopper. A pinch clamp and high-vacuum silicone grease were used to ensure hermetic seal. The assembly was heated in either a stirred oil bath or an air oven and kept at 90 °C for 90 min unless otherwise specified. After conversion, the PbI\(_2\) films were removed from the still hot flask.

**Conversion of PbI\(_2\) to CH\(_3\)NH\(_3\)PbI\(_3\).** CH\(_3\)NH\(_3\)I was synthesized by adding hydroiodic acid (55%, no stabilizer; Sigma-Aldrich) dropwise to a methyamine solution (TCI, 40% in methanol) that was stirred and kept in an ice-bath. Methanol and water were evaporated with a rotary evaporator, leaving yellow crystals of the raw compound. The raw compound was recrystallized in ethanol. The resulting white crystals were separated by filtering, washed with tetrahydrofuran as well as diethyl ether, and then dried. Dry CH\(_3\)NH\(_3\)I was kept in a N\(_2\) glovebox (<0.5 ppm of O\(_2\) and H\(_2\)O).

Conversion of PbI\(_2\) to MAPbI\(_3\) was carried out in an assembly similar to the one used for the PbO\(_2\) to PbI\(_2\) conversion, with stopcock adapter instead of glass stopper. No silica gel was used, and the boat was loaded with 100 mg of CH\(_3\)NH\(_3\)I instead of hydroiodic acid. The flask was evacuated with a rotary pump to a pressure of 0.9 mbar before heating to 180 °C by means of either a stirred oil bath or an air oven. Unless otherwise stated, the flask was kept at 180 °C for 2 h. To avoid CH\(_3\)NH\(_3\)I condensation, the MAPbI\(_3\) films were taken out of the flask immediately after the flask was removed from the hot oil or oven.

**Characterization.** The morphology of the films was studied by FESEM using a Hitachi S-4800 instrument. The composition of the films was studied by energy-dispersive X-ray (EDX) spectroscopy with an Oxford INCA 350 energy spectrometer connected to the FESEM instrument. The films thicknesses were calculated from the EDX data with GMRFilm software\(^{59}\) using bulk densities. All of the reported thicknesses are mean values of five measurements from distinct positions across the film. The thickness errors are standard deviations of these five measurements.

AFM images for analyzing the surface roughness and morphology were recorded using a Veeco Multimode V AFM with a Nanoscope V controller. The images were captured in the tapping mode (intermittent contact mode) in air using silicon probes, with a nominal tip radius of 8 nm and a nominal spring constant of 40 N/m (RTESP from Bruker). Image analysis was performed with Gwyddion software.\(^{60}\) The images were plane-fitted to remove artifacts caused by sample tilt and scanner bow. Roughness was calculated as an rms value (or Rq) from \(5 \times 5 \mu\text{m}^2\) images for all films. For grain size evaluation, grains were identified by a watershed algorithm from \(5 \times 5 \mu\text{m}^2\) images for PbI\(_2\) and MAPbI\(_3\) films, whereas for PbO\(_2\) films, 0.5 \(\times 0.5 \mu\text{m}^2\) images were used due to the small size of the grains. The grain size was calculated as the median diameter of circles with areas equivalent to the area of the identified grains.

The crystallinity of the film was studied with a PANalytical X’Pert Pro MPD diffractometer using Cu Kα-radiation. XRD patterns were measured using both grazing incidence (GIXRD, incident angle 1°) and \(\theta−2\theta\) geometries. Transmittance measurements in the UV-vis range were performed with a Hitachi U2000 spectrophotometer. Optical band gaps were evaluated from the transmittance data and Tauc plots according to the approach described in the literature.\(^{61,62}\) The band gaps of PbI\(_2\) and MAPbI\(_3\) were assumed to be direct-allowed and that of PbO\(_2\) indirect-allowed.

**I−V** measurements were carried out with a Keithley 2400 Source Meter, using a step width of 0.05 V and a source step delay of 0.1 s. Electrical contacts were made by applying Ga–In eutectic alloy (Sigma-Aldrich) dots (ca. 3 mm\(^2\)) to FTO and MAPbI\(_3\) and contacting these dots with needle probes. A halogen spot lamp (50 W) was used for illumination.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00351.

Two different PbO\(_2\) ED bath geometries and their effect on PbO\(_2\) the film thickness profile (Figure S1); comparison of PbO\(_2\) film thickness profiles obtained from different ED baths (Figure S2); comparison of ED-based processes for MAPbI\(_3\) films reported in the literature and in this work (Table S1); iodine content in the films at different stages of the PbO\(_2\) to PbI\(_2\) conversion (Figure S3); X-ray diffractograms of the films at different stages of the PbO\(_2\) to PbI\(_2\) conversion (Figure S4); UV-vis transmittance of the films at different stages of the PbO\(_2\) to PbI\(_2\) conversion (Figure S5); X-ray diffractograms of the as-deposited PbO\(_2\) film, the PbO\(_2\) film converted to the PbI\(_2\) film, and the PbI\(_2\) film converted to the MAPbI\(_3\) film (Figure S6); crystal structure of PbI\(_2\) with (001) and (110) planes visualized (Figure S7); photograph of the reactor used for converting PbI\(_2\) films into MAPbI\(_3\) (Figure S8); X-ray diffractograms of the films at different stages of the PbI\(_2\) to MAPbI\(_3\) conversion (Figure S9); iodine content in the films at different stages of the PbI\(_2\) to MAPbI\(_3\) conversion (Figure S10); UV-vis transmittance of the films at different stages of the PbI\(_2\) to MAPbI\(_3\) conversion (Figure S11); I−V curves of the β-MAPbI\(_3\) film with and without illumination and the setup used for electrical measurements (Figure S12); X-ray diffractogram of the PbI\(_2\) film converted with FAI and its FESEM image (Figure S13) (PDF)

Recorded conversion of an electrodeposited PbO\(_2\) film (at 0.25 mA cm\(^{-2}\)) for 100 s) into PbI\(_2\) (Video S1) (MPG)

Recorded conversion of a PbI\(_2\) film into MAPbI\(_3\). The PbI\(_2\) film was obtained by converting the PbO\(_2\) film electrodeposited at 0.25 mA cm\(^{-2}\) for 725 s (Video S2) (MPG)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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