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Drop-Casting Method to Screen Ruddlesden–Popper Perovskite Formulations for Use in Solar Cells

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ABSTRACT: Small-area metal—halide perovskite solar cells (PSCs) having power-conversion efficiencies (PCEs) of greater than 25% can be prepared by using a spin-coated perovskite layer, but this technique is not readily transferrable to large-scale manufacturing. Drop-casting is a simple alternative method for film formation that is more closely aligned to industry-relevant coating processes. In the present work, drop-casting was used to prepare films for screening two-dimensional Ruddlesden—Popper (2DRP) metal—halide perovskite formulations for potential utility in PSCs, without additional processing steps such as inert-gas blowing or application of antisolvent. The composition of the 2DRP formulation used for drop-casting was found to have a profound effect on optical, spectroscopic, morphological, and phase-distribution properties of the films as well as the photovoltaic performance of related PSC devices. This facile method for screening film quality greatly assists in speeding up the identification of perovskite formulations of interest. The optimal 2DRP perovskite formulation identified from screening was utilized for industry-relevant one-step roll-to-roll slot-die coating on a flexible plastic substrate, producing PSCs having PCEs of up to 8.8%. A mechanism describing film formation and phase distribution in the films is also proposed.

KEYWORDS: drop-casting, self-spreading, slot-die coating, two-dimensional perovskite, printable perovskite solar cells

INTRODUCTION

Inorganic–organic metal–halide perovskite solar cells (PSCs) are promising candidates for future use in photovoltaic devices due to their low cost, low processing temperature, and high power-conversion efficiency (PCE).^{1–3} Various solution-deposition methods are available for fabrication of the perovskite layer, and optimization of these methods is critical for obtaining high-performance PSCs. Examples of methods used for lab-scale solution deposition of perovskite layers for PSCs are illustrated in Figure 1.

Spin-coating is the most commonly used laboratory method for producing the perovskite layer and has resulted in PSCs having PCEs of more than 25%.⁴ It is a conveniently simple approach for fabricating lab-scale devices but results in most of the solution being spun off the substrate leading to substantial material waste. It is also impractical for achieving uniform large-area films. Furthermore, the drying kinetics of spincoated solutions is much faster than other conventional industrial coating methods due to the combination of centrifugal force and gas flow caused by the spinning substrate, making the direct translation of spin-coated perovskite formulations to large-scale coating methods extremely difficult. Consequently, spin-coating is generally considered unsuitable for producing large-area PSC devices at an industrial scale.

A variety of spin-coating-free methods have been developed to prepare PSCs, including vapor deposition,⁵ screen printing,^{6,7} blade coating,⁸ slot-die coating,^{9,10} and meniscusassisted solution printing.¹¹ An advantage of the vapor deposition method is that it avoids the use of solvent, but it

Received:September 10, 2021Accepted:November 2, 2021Published:November 16, 2021







Figure 1. Illustration of spin-coating (a), drop-casting (b), and slotdie coating (c) methods of perovskite film formation. In contrast to the spin-coating process, for lab-scale drop-casting and slot-die coating the substrate is typically stationary, and while the deposited solutions can be allowed to dry naturally, heating the substrates and/ or blow-drying with air or nitrogen is sometimes used to accelerate solvent evaporation.

requires a complicated high-vacuum apparatus, making it unsuitable for low-cost mass production. Screen-printing, blade-coating, and slot-die coating are all potentially scalable methods for fabrication of PSCs, but slot-die coating has the advantages of low material wastage, ease of patterning, and suitability for continuous processing.^{12–15} Perovskite solar cells incorporating a slot-die-coated perovskite layer having PCEs exceeding 20% have been reported,¹⁶ although the extra processing steps of applying antisolvent or high-pressure gas blowing were used to optimize the morphology of the perovskite film in these cases. Preparing perovskite films in a one-step process without the assistance of antisolvent or gasblowing can significantly reduce cost and improve batch-tobatch reproducibility of the process. However, these so-called "naturally dried" perovskite films often exhibit undesirable morphological characteristics such as severely rough surfaces and pinholes, leading to poor device performance.

Identifying suitable perovskite materials that form highquality films via natural drying requires substantial effort due to the wide variety of available perovskite compositions, including inorganic perovskites,¹⁷ mixed-cation perovskites,¹⁸ mixed tin/ lead perovskites,¹⁹ and 2D/3D perovskites.^{20–23} The perovskite composition, solvents, and additives all have a strong influence on the crystallization process and, ultimately, film quality. Acceleration of the upscaling of PSC technology requires the development of a facile method through which suitability of potential materials and preparation conditions for large-scale coating can be assessed quickly.

Recently, we reported a drop-casting method to prepare inorganic–organic hybrid lead–halide perovskite films for $PSCs^{24-29}$ where the perovskite solution spreads spontaneously on a heated substrate to form uniformly smooth, high-quality perovskite films upon drying. The self-spreading in the drop-casting method is caused by the unbalanced surface tension of solution/substrate, solution/air, and air/substrate

interfaces, enabling film preparation without assistance of depositing apparatus.²⁹ Apart from conserving time and materials, the drop-casting method is, in principle, much more like an industry-relevant coating processes, especially slot-die coating, than spin-coating. The similarity in the fluid dynamics and drying kinetics of films produced by using the drop-cast and slot-die methods from a given precursor formulation²⁴ means that the film formation behavior observed in the drop-casting method can provide a good indication of film formation by using the more technically complex slot-die coating method. For example, we previously found very little difference in the average PCE of PSC devices comprising a perovskite layer formed by drop-casting or slot-die coating the two-dimensional Ruddlesden-Popper (2DRP) perovskite formulation $BA_2MA_3Pb_4I_{13}$ (BA = *n*-butylammonium cation, MA = methylammonium cation).²⁴

Because the performance of PSCs comprising a slot-diecoated perovskite layer is highly sensitive to a variety of parameters, such as perovskite composition, solvent, additives, and coating conditions,³⁰ the comparative simplicity of the drop-cast method offers an attractive means of simplifying and accelerating the process of identifying optimal perovskite formulations and coating conditions. Identifying further perovskite formulations suitable for slot-die coating will provide greater choice and better performance for the wide variety of potential end-use applications of PSC technology.

Herein, we report the results of a systematic approach for screening an array of 2D organic-inorganic hybrid lead-halide 2DRP perovskite formulations comprising a set of straightchain alkylammonium cations, based on analyzing simple dropcast films by using routine optical, spectroscopic, microscopic, and electrical techniques. This class of perovskites is of interest due to their superior environmental stability and unique optoelectronic properties.³¹ This screening process resulted in a substantially smaller subset of formulations of potential interest, with the reliability of the screening verified by measurements of device PCE. A film-formation mechanism is proposed that is consistent with the observed film morphologies and phase distributions. The perovskite formulation having the highest PCE determined from the drop-cast film screening process was utilized to prepare PSCs on a flexible plastic substrate by using industry-relevant onestep R2R slot-die coating of the perovskite layer.

EXPERIMENTAL DETAILS

Solution Preparation. The MAPbI₃ precursor solution was prepared by dissolving 0.3 M PbI₂ (Alfa Aesar) and 0.3 M MAI (Greatcell Solar) in dimethylformamide (DMF) (Sigma-Aldrich). Precursor solutions for 2D perovskites $X_2MA_3Pb_4I_{13}$ with concentrations of 0.3 M of Pb²⁺ were prepared in DMF. The molar ratio of the reagents PbI₂:MAI:C_mAI (Greatcell Solar) was 4:3:2. Precursor solutions for (C₄A)₂MA_{n-1}Pb_nI_{3n+1} perovskites were prepared by fixing the Pb²⁺ concentration at 0.3 M; the concentrations of MAI and (C₄A)I can be calculated by using the *n* value. The precursor solutions were stirred at 70 °C for 1 h. The PEDOT:PSS solution for the R2R slot-die process was made by mixing 1 mL of PEDOT:PSS (HC Starck, Baytron P Al 4083), 1 mL of deionized water, and 1.6 mL of isopropanol.

Materials Characterization. Photographs of the films were taken with an Epson Perfection V700 photoscanner. The SEM images were taken with a Zeiss Merlin field emission SEM (FE-SEM) operated at an accelerating voltage of 5 kV. Optical microscopy images were taken by a LW200-3JT microscope. UV–vis absorption spectra were recorded by a Lambda 35 PerkinElmer absorption spectrometer.

Steady-state PL emission spectra were recorded by a luminescence spectrometer (Edinburgh Instruments, FLSP920).

Device Fabrication Using the Drop-Casting Method. The perovskite and charge transport layers were prepared in air with humidity between 30% and 50%. Patterned ITO glass was cleaned in detergent (Deconex12PA detergent solution), deionized water, acetone, and isopropanol sequentially by ultrasonication and then treated with UV-ozone for 15 min. PEDOT:PSS was spin-coated at 5000 rpm for 30 s. The substrate was then heated on a hot plate at 150 °C for 10 min in air. After cooling to room temperature, the substrate was heated on a 60 °C hot plate for 2 min, and then 6 μ L of perovskite solutions was dropped onto the center of the 25 mm \times 25 mm substrate. The solution spontaneously spread on the substrate and dried in 1 min, forming a round black film. The substrate was then heated at 100 $^{\circ}$ C for 2 min. PC₆₁BM in chloroform with a concentration of 10 mg mL⁻¹ was spin-coated onto the perovskite layer at 1000 rpm for 30 s. Then PEIE (0.05% w/w in isopropanol) was spin-coated onto the $PC_{61}BM$ layer at 4000 rpm for 30 s. Finally, 100 nm Ag was evaporated through a shadow mask to give an active area of 0.1 cm².

Device Fabrication Using the Roll-to-Roll Process. The setup of the slot-die roll-to-roll coating system and the coating of the PEDOT:PSS layer can be found in our previous work.²⁴ A $(C_4A)_2(MA)_4Pb_5I_{16}$ precursor solution containing 0.6 M Pb²⁺ was used. The speed of the substrate movement was 0.5 m min⁻¹, and the solution feed speed was 30 μ L min⁻¹. The coated film was passed over the first curved hot plate at 60 °C to dry the film, and then over a second hot plate at 100 °C, before being collected in a roll. After completion of the perovskite layer, the substrate was cut into 25 mm × 25 mm to make solar cells. PC₆₁BM, PEIE, and Ag layers were deposited as described above.

Device Measurements. The J-V curves were measured under an inert atmosphere by using a Keithley 2400 source meter under standard solar irradiation (AM 1.5G, 100 mW cm⁻²). The light intensity was calibrated by using a reference cell (Hamamatsu S1133 with KG5 filter, 2.8 × 2.4 mm² of photosensitive area), which was calibrated by a certified reference cell (PV Measurements, certified by NREL) under 1000 W m⁻² AM 1.5G illumination from an Oriel AAA solar simulator fitted with a 1000 W Xe lamp.

RESULTS AND DISCUSSION

The size of the bulky organic cations (typically alkylammonium cations), R_{1} , and/or the value of n_{1} in 2DRP perovskite compositions, $R_2MA_{n-1}Pb_nI_{3n+1}$, have been shown to have a major influence on the optical and optoelectronic properties of spin-cast 2DRP perovskite films.³² This is reflected in the crystal growth and orientation, passivation of trap states, and hindering of ion motion.³³ Identifying the combination of size of R and value of n giving optimal perovskite film properties for PSCs requires the screening of the potentially large array of 2DRP perovskite formulations generated by systematically changing the cation size and n value. In this work, the cation size was varied through the use of straight-chain alkylammonium ions having different chain lengths. For this purpose, a set of the 2DRP perovskite formulations $(C_mA)_2MA_{n-1}Pb_nI_{3n+1}$ were prepared by using dimethylformamide (DMF) as the solvent, where MA is the methylammonium cation and C_mA represents a homologous series of linear straight-chain alkylammonium cations with m being the number of carbon atoms in alkyl chain. The alkylammonium salts used in this work, and their abbreviations, are shown in Figure 2. When the carbon chains in C_mA are longer than m = 6, charge transport in the 2DRP perovskite is hindered due to the insulating property of the carbon chains, which may lead to inferior photovoltaic performance. If n is too large, the concentration of 2DRP phases in the film becomes much lower than the 3D perovskite phase,²¹ reducing the potential beneficial effects of





the 2D phases. Consequently, the array of 2DRP formulations studied in this work was restricted to those having $m \le 6$ and $n \le 8$.

Drop-casting provides a straightforward means for rapidly preparing films from 2DRP perovskite formulations in the required parameter space. The images of the drop-cast perovskite films prepared from the set of precursor solution compositions shown in Figure 3a illustrate the significant influence of the solution formulation on the visual appearance of the dry films. Considering initially the top row of images in Figure 3a, the film formed by using the $\{m = 2, n = 4\}$ formulation is a hazy, gray color with a very rough and nonuniform surface, similar to the 3D MAPbI₃ film. The significant light scattering by this film is the origin of the elevated baseline in its UV-vis absorption spectrum, where the "baseline" is taken here to be the absorbance at 800 nm which is beyond the bandgap of 3D perovskite (Figure 3b). In contrast, the brown films prepared from the $\{m = 3-5, n = 4\}$ formulations are relatively glossy with minimal haze as seen in the lower baselines in their UV-vis absorption spectra. Uniform, compact crystalline grains in the perovskite layer are a prerequisite for a PSC device to display good photovoltaic performance,^{2,3} and these physical properties typically yield this type of glossy film showing a high degree of specular reflectance. The brown film obtained by using the $\{m\}$ = 6, n = 4 formulation has a high degree of haze, as seen in its elevated UV-vis absorption baseline.

The strong dependence of perovskite film color on *n* seen in the second row of images in Figure 3a arises from contributions to optical absorbance by constituent perovskite phases having different dimensionalities as defined by the number of Pb-I octahedron layers in their crystal structure. The bandgap of the perovskite phases decreases (red-shifts) with increasing dimensionality.³⁴ The multitude of bands in the UV-vis absorption spectra of the drop-cast films (Figures 3b,c) show that perovskite phases having a variety of dimensionality exist in the films. The glossy film obtained by using the $\{m = 4, n = 1\}$ formulation shows high specular reflectance implying uniform, compact grains and displays one sharp peak associated with a phase consisting of a single layer of Pb-I octahedrons; the phase purity of this film is expected because no other phases are stoichiometrically possible in a solution of this formulation. The two sharp absorption bands seen for the highly colored and reflective film from the $\{m = 4, \dots, m = 4\}$ n = 2 formulation indicate the presence of perovskite phases containing one or two layers of Pb-I octahedrons. The weaker, broad, highly red-shifted band at around 750 nm is associated with a quasi-3D $(n \rightarrow \infty)$ phase, indicating a degree of disproportionation has occurred in this stoichiometrically n

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Figure 3. (a) Images of films drop-cast from solutions of MAPbI₃, $(C_mA)_2MA_3Pb_4I_{13}$, or $(C_4A)_2MA_{n-1}Pb_nI_{3n+1}$ in DMF and UV-visible absorbance spectra of drop-cast films from solutions of $(C_mA)_2MA_3Pb_4I_{13}$ (b) and $(C_4A)_2MA_{n-1}Pb_nI_{3n+1}$ (c) in DMF. Size of substrates in (a): 25 mm × 25 mm. Peak numbering corresponds to the number of Pb–I octahedron layers in the absorbing 2DRP phases in the films.



Figure 4. (a) SEM images of films drop-cast from solutions of MAPbI₃, $(C_mA)_2MA_3Pb_4I_{13}$, and $(C_4A)_2MA_{n-1}Pb_nI_{3n+1}$ in DMF and J-V curves for perovskite solar cells comprising a drop-cast layer using solutions of $(C_mA)_2MA_3Pb_4I_{13}$ (b) or $(C_4A)_2MA_{n-1}Pb_nI_{3n+1}$ (c) in DMF. Scale bar: 2 μ m.

= 2 formulation. The brown films formed from the $\{m = 4, n = 3-5\}$ formulations show high specular reflectance with minimal light scattering, suggesting uniform compact grains, and their UV-vis absorption spectra indicate the presence of a variety of low-dimensional and high-dimensional (quasi-3D) perovskite phases. The films from the $\{m = 4, n > 5\}$ formulations are nonuniform with a relatively high degree of

light scattering and, as expected, progressively come to more closely resemble the 3D MAPbI₃ film with increasing *n* value; the gray color of the film from the $\{m = 4, n = 8\}$ formulation and its UV–vis absorption spectrum are consistent with the presence of a considerable fraction of quasi-3D perovskite phases.

The SEM images in Figure 4a demonstrate the significant role of the chain length in the bulky linear-chain alkylammonium cations in determining grain morphology in the drop-cast films. As seen in the top row of images, the $\{m = 2, n = 4\}$ formulation produces a film comprising large approximately circular grains and the films from $\{m = 3-5, n = 4\}$ formulations appear to consist of small relatively compact grains, whereas holes and cracks can be seen in the film from the $\{m = 6, n = 4\}$ formulation. This trend correlates closely with that of the optical characteristics described above, where the films for the $\{m = 3-5, n = 4\}$ formulations display higher specular reflectance and lower light scattering than the other two *m* values.

The second row of SEM images in Figure 4a also show that compact perovskite grain morphology is produced for films from the $\{m = 4, n = 1-5\}$ formulations, whereas large gaps between larger grains are observed for the films of the $\{m = 4, n = 6-8\}$ formulations. This trend correlates closely with that of the optical characteristics described above, where films from the $\{m = 4, n = 1-5\}$ formulations display higher specular reflectance and lower light scattering.

The needle-like grains seen in the SEM image of the dropcast 3D MAPbI₃ perovskite film are similar to those reported for spin-cast MAPbI₃ films produced without use of antisolvent or additives.³⁵ Despite the similarity in the optical characteristics of the film from the {m = 4, n = 8} formulation and the MAPbI₃ perovskite films, the presence of the C4 alkylammonium cation in the 2DRP perovskite formulation evidently results in a significantly different grain morphology to that in the 3D MAPbI₃ film, suggesting that the bulky alkylammonium cations disrupts the growth of the needle-like MAPbI₃ crystals.

The next step of the screening process involves verification that the optical and morphological trends observed in the drop-cast films translate to the photovoltaic (PV) performance of PSCs. Perovskite layers drop-cast from $(C_mA)_2MA_{n-1}Pb_nI_{3n+1}$ solutions were incorporated as the light-absorbing layer in devices having the architecture ITO/ PEDOT:PSS/perovskite/PC₆₁BM/PEIE/Ag, where all solution-processed layers were fabricated in air under ambient laboratory conditions (see the Experimental Details section). Considering first the effect of *m* on the PV performance, it can be seen from the results in Figure 4b and Table S1 that the devices comprising a drop-cast layer of the $\{m = 2, n = 4\}$ formulation perform poorly, consistent with its optical and morphological characteristics described above. Devices comprising a perovskite layer based on bulkier alkylammonium cations with m = 3-5 showed significantly higher PCE, consistent with their more favorable grain morphology. Increasing the size of the bulky cation further to m > 5 results in loss of PCE and electrical shorting, attributed to the presence of the pinholes seen in the perovskite layer in Figure 4a. This dependence of PV performance on m correlates very well with the trends in the optical properties and grain morphology of the drop-cast films. It was also found that the rings on the films shown in Figure 3 have a negligible impact on PCE.

The effect of the magnitude of n on PV performance of devices comprising a drop-cast layer of the $(C_4A)_2MA_{n-1}Pb_nI_{3n+1}$ formulation can be seen in Figure 4c and Table S2. The poor PV performance of the device produced with $n \leq 2$ is ascribed to the large optical bandgaps of 2DRP phases in these films, as seen in their UV-vis absorption spectra (Figure 3c). Perovskite layers made by

using n = 3-5 formulations give devices showing the highest PCE, consistent with their compact film morphology as show in Figure 4a. The optimized thicknesses of the perovskite layers are ~350 nm. Significantly lower PCEs were obtained for devices based on formulations having n = 6 or 8, which is attributed to shorting caused by pinholes in the perovskite layer. Little hysteresis was observed in the J-V curves measured in forward and reverse scans (Figure S1), and the steady-state PCE of the "champion" cell ($\{m = 4, n = 5\}$ formulation) recorded by using maximum power point (MPP) tracking (Figure S2) of 15.04% is consistent with the J-V measurement. As expected from the film morphology of the drop-cast MAPbI₃ film, PSCs comprising a drop-cast layer of MAPbI₃ showed extremely poor PV performance.

The excellent self-consistency between the PV performance of the PSC devices and the optical and morphological characteristics of their corresponding drop-cast films provides good evidence for the reliability of this facile screening process.

Observation of the crystal growth process in situ was attempted by using optical microscopy to better understand the origin of the formulation-dependent film morphologies. Direct in situ measurement of crystal growth in the drop-cast films is facilitated by the inherently high environmental stability of the method used in this work, which enables a simple experimental setup. Images of the crystal growth in a MAPbI₃ film recorded at different time intervals after dropcasting (Figure S3) show long needle-like grains emanating from small seed crystals and anisotropic growth of the seed crystals leading to nonuniform grain morphology (Figure 4a). However, attempts to monitor the crystal growth of films formed from the 2DRP perovskite formulations of interest arising from the screening process were thwarted due to the grains being too small to resolve by using the optical microscope (Figure S4). Nevertheless, the presence of the bulky alkylammonium cations clearly hinders the development of the needle-like crystals normally observed for MAPbI₃ films and leads to uniform grains having substantially reduced size. In the MAPbI₃ perovskite solution, crystals can grow in any direction from the nucleus due to its symmetrical structure. Unlike MAPbI₃, in the DMF solutions containing $(C_mA)_2MA_{n-1}Pb_nI_{3n+1}$, the bulky alkylammonium cations, Pb^{2+} , and I⁻ can only form a layered structure comprising Pb-I octahedrons layers and bulky ammonium cation layers. A film-formation mechanism consistent with the observed influence of the various bulky alkylammonium cations on the perovskite grain morphology is illustrated in Figure 5.

The growth of MAPbI₃ crystals is terminated if the ammonium groups of the bulky C_mA cations bond to the MAPbI₃ nuclei. Interaction of the nonpolar alkyl groups of C_mA cations outside the nucleus with alkyl groups of neighboring C_mA cations allows additional MAPbI₃ layers to grow from the nucleus. Consequently, the presence of the bulky alkylammonium cations results in two orthogonal crystal growth directions: one resulting in the lateral expansion of the Pb–I octahedron sheets between the bulky ammonium cations and the other leading to an increase in the number of Pb–I octahedron layers (i.e., dimensionality) in the 2DRP structure. The interaction forces between the bulky alkylammonium cations are expected to strongly influence the relative rates of growth of the layered structure in these directions, leading to different grain morphologies.

The photoluminescence (PL) emission spectra recorded for drop-cast films formed by using $(C_4A)_2MA_{n-1}Pb_nI_{3n+1}$



Figure 5. Illustrations of crystal growth in the solution of $MAPbI_3$ perovskite and 2DRP perovskites containing bulky cations (a), the solute concentration gradient in the solution caused by solvent evaporation (b), and large cations (e.g., C_mA) in the solution of 2DRP perovskite formulations (c).

formulations are shown in Figure 6 as a function of n. Like the UV-vis absorption spectra of the drop-cast films, the PL spectra of these films also display bands signaling the presence of a variety of 2DRP perovskite phases (Figure 5). The film produced by using the n = 1 formulation displays a single, strong, sharp PL band irrespective of which side is probed, confirming that this film comprises solely 2DRP perovskite phase comprising a single Pb-I octahedron layer. While various mechanisms have been proposed to describe the phase distribution in films produced by using 2DRP perovskite formulations, $^{36-38}$ the general consensus is that the 3D or quasi-3D perovskite phases initially form at the air-liquid interface during the drying process, with the bulky alkylammonium cations forced toward the substrate-liquid interface where there is preferential formation of lowerdimensional perovskite phases.³⁷ However, the complete absence of the broad, red-shifted PL band at \geq 750 nm associated with quasi-3D perovskite phases for films produced from $(C_4A)_2MA_{n-1}Pb_nI_{3n+1}$ formulations having n < 4 is intriguing (Figure 6).

Evaporation of solvent initially causes a higher solute concentration at the air-liquid interface than in the bulk solution, as illustrated in Figure 5b. Consequently, crystal nucleation and growth tend to begin at the air-liquid surface.



Figure 6. PL emission spectra of films drop-cast from solutions of $(C_4A)_2MA_{n-1}Pb_nI_{3n+1}$ in DMF, as a function of *n*. Peak numbering corresponds to the number of Pb–I octahedron layers in the various 2DRP phases in the films. Samples consisted of glass/PEDOT:PSS/perovskite. Excitation and emission detection by using the perovskite (front) side or the glass (back) side, as indicated (excitation wavelength: 440 nm).

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Figure 7. (a) Illustration of the roll-to-roll slot-die process for preparation of perovskite films on flexible substrate. (b) J-V curve of a perovskite solar cell prepared by using a layer of roll-to-roll slot-die-coated (C₄A)₂MA₄Pb₅I₁₆ perovskite formulation on flexible PET/ITO substrate (inset: photo of the slot-die-coated perovskite film).

A critical MA:C_mA molar ratio in the 2DRP perovskite formulation appears to exist, below which the formation of low-dimensional perovskite phases dominates. In the specific case of C₄A cations, the critical MA:C₄A ratio is found to be 2, with higher-dimensional quasi-3D phases observed only when $n \geq 4$. For example, for $(C_4A)_2MA_{n-1}Pb_nI_{3n+1}$ formulations with $n \ge 4$, the initial concentration of MA in the drop-cast solution is at least twice that of C4A, and in this case the quasi-3D perovskite phases appear to have a competitive advantage for formation at the air-liquid interface. The resulting higher depletion rate of MA than C₄A at this interface then leads to a concomitant decrease in the MA:C4A ratio in the bulk solution, resulting in enhanced formation of low-dimensional phases once the MA:C4A ratio falls below 2. A prominent redshifted PL emission band centered around 760 nm, associated with the quasi-3D phases, is seen in the spectra of films from the formulations with $n \ge 4$ irrespective of which side of the sample is probed, indicating that the quasi-3D phase perovskites are distributed throughout the drop-cast film. In contrast, the absence of PL emission from low-dimensional perovskite phases upon excitation and detection from the perovskite side of the sample confirms that these phases are concentrated more closely to the glass-perovskite interface. Notably, when n = 8, the excess concentration of MA over C₄A throughout the film forming process appears to be sufficiently large to completely suppress the formation of low-dimensional phases.

The spectral distribution of PL emission from drop-cast films of $(C_m A)_2 M A_3 P b_4 I_{13}$ (*n* = 4) formulations was found to be essentially independent of the size of the C_mA cation, with the exception of the m = 2 (ethylammonium) cation (Figure S5). The absence of PL bands and UV-vis absorption bands associated with low-dimensional phases for this film indicates that it comprises only quasi-3D perovskite phases, suggesting that the C₂A cation is not sufficiently bulky to induce the formation of a low-dimensional perovskite phase. Unlike the other perovskite films, perovskite film prepared by using C₈A shows Ruddlesden–Popper perovskite structures (n = 2, n = 3) both at the surface and bottom of the film (Figure S5f). This may be attributed to the long hydrophobic carbon chain which is capable of dwelling at the surface of the solution acting similar to the surface surfactant (Figure 5c), leading to the increased concentration of C₈A at the surface and in turn inducing the formation of Ruddlesden-Popper perovskites.

A comparison of the trends in device PV performance in Tables S1 and S2 and the perovskite phase information obtained from PL and UV-vis absorption spectroscopy

suggests that the coexistence of a mixture of lower- and higher-dimensional (quasi-3D) perovskite phases in the dropcast films may be important for good device performance. Apart from the benefits to grain morphology described above, charge transport in low-dimensional perovskite phases alone is known to be highly dependent on crystal orientation,³⁸ and so it may be that their coexistence with quasi-3D perovskite phases boosts the efficiency of transportation of charge carriers to the electrodes, leading to improved device performance.

The results of the screening method described above indicate that the drop-cast film displaying the best overall characteristics was produced by using the (C4A)2MA4Pb5I16 formulation (m = 4, n = 5). The PV performance of this optimal formulation was, therefore, evaluated as a slot-die coating on a flexible substrate by using a roll-to-roll (R2R) process (Figure 7a). Two hot plates were used to heat the film, as was the case for drop-casting. A first hot plate at 60 °C was used to dry the film (see Figure S6), followed by a second hot plate at 100 °C for thermal annealing. A photo of the R2R slotdie-coated perovskite film on the flexible PET/ITO substrate is shown in the inset of Figure 7b. As found for the drop-cast film, the R2R slot-die-coated film shows a uniformly high specular reflectance and is pinhole-free, with a thickness of ~350 nm. Perovskite solar cells were prepared by using this slot-die-coated perovskite film, yielding a "champion" cell with $V_{oc} = 1.08 \text{ V}, J_{sc} = -15.58 \text{ mA/cm}^2$, FF = 52.02%, and PCE = 8.75% (Figure 7b). Although this PCE is comparable with other values reported for devices based on R2R-coated perovskites,²⁹ it is substantially lower than that of the cells having the same active area prepared by using a drop-cast layer of the same 2DRP perovskite formulation on glass/ITO substrates (Tables S2 and S3). This is attributed to the substantially higher sheet resistance and roughness of the flexible PET/ITO substrate than the glass/ITO substrates.

CONCLUSIONS

In summary, simple drop-cast film preparation under ambient laboratory conditions, coupled with visual inspection and routine optical, microscopy, and electrical measurements, was shown to provide a facile method for effectively screening an array of 2D organic—inorganic hybrid lead—halide Ruddlesden—Popper perovskite formulations for their potential to form high quality films for use in solar cells. A mechanism was proposed to explain the dependence of perovskite grain morphology and distribution of the multidimensional perovskite phases on the 2DRP perovskite formulation used for drop-casting.

Screening of drop-cast films enabled the number of compositions of potential interest to be substantially reduced. Ultimately, the optimally performing formulation was verified by fabricating and testing devices, but screening meant that the number of devices needing to be evaluated in this final step was greatly reduced. The similarity between the drying mechanisms for drop-cast and slot-die coated films, and the greater simplicity of the drop-cast method, means that this screening offers a quick and useful guide to likely quality of a slot-diecoated film for a given 2DRP perovskite formulation. The drop-casting method has the merit of simpleness, with the demerit of scalability. The compatibility of the drop-casting with slot-die coating effectively makes up the demerit.

The optimal formulation identified through the screening process was evaluated for roll-to-roll fabrication of solar cells on a flexible plastic substrate by using an industrially relevant one-step slot-die process to deposit the perovskite formulation under ambient laboratory conditions. This produced uniform, compact perovskite films, with a champion device PCE of 8.8%. The higher sheet resistance and surface roughness of the underlying flexible PET/ITO substrate are likely to be responsible for the PCE being substantially lower than that for devices comprising a drop-cast layer of the same perovskite formulation on a glass/ITO substrate.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c17475.

J-V curves obtained by forward and reverse scan; PCE for the "champion" cell obtained by using MPP tracking; *in situ* optical microscope images for MAPbI₃ crystal growth process; PL emission spectra of films drop-cast from solutions of $(C_mA)_2MA_3Pb_4I_{13}$ in DMF as a function of *m*; photograph showing the drying of the R2R slot-die-coated solution; performance data of solar cells (PDF)

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Notes

The authors declare no competing financial interest.

Research Article

ACKNOWLEDGMENTS

The authors acknowledge the financial support from the Australian Government through the Australian Renewable Energy Agency (ARENA). Responsibility for the views, information, or advice expressed herein is not accepted by the Australian Government. C.Z. acknowledges the support of the Australian Centre for Advanced Photovoltaics (ACAP) Postdoctoral Fellowships. M.G. and A.D.S. acknowledge the Devices and Engineering System program of CSIRO Manufacturing.

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