Simple Method for Efficient Slot-Die Coating of MAPbI₃ Perovskite Thin Films in Ambient Air Conditions

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ABSTRACT: Scalable methods for deposition of lead halide perovskite thin films are required to enable commercialization of the highly promising perovskite photovoltaics. Here, we have developed a slot-die coating process under ambient conditions for methylammonium lead iodide (MAPbI₃) perovskite on heated substrates (about 90 °C on the substrate surface). Dense, highly crystalline perovskite films with large grains (100–200 μm) were obtained by careful adjustment of the deposition parameters, using solutions that are similar but more dilute than those used in typical spin-coating procedures. Without any further after treatments, such as antisolvent treatment or vapor annealing, we achieved power conversion efficiencies up of 14.5% for devices with the following structure: conducting tin oxide glass (FTO)/TiO₂/MAPbI₃/spiro-MeOTAD/Au. The performance was limited by the significant roughness of the deposited films, resulting from the hot-casting method, and the relatively high deposition temperature, which led to a defect-rich surface due to loss of MAI.

KEYWORDS: slot-die coating, perovskite solar cells, grain size, scalable deposition techniques, hot casting

INTRODUCTION

Large-scale implementation of renewable energy is highly needed to reduce the carbon footprint of energy production and to meet the growing energy demand in our society today. Photovoltaics efficiently harvest solar energy and can significantly contribute to electricity production worldwide, thereby replacing polluting fossil fuels. The novel and highly performing perovskite photovoltaic technology has the potential to make a significant impact in the field and will be commercialized in the very near future.¹

Lead halide-based perovskite solar cell have undergone a remarkable increase in power conversion efficiency (PCE) in a short period of time, from 3.8% reported in 2009⁷ to 25.2% in 2019⁹, making this technology a serious competitor to the market dominating silicon-based photovoltaics. A wide variety of deposition techniques is available for perovskites, ranging from solution-based processes to vacuum evaporation.⁸ Spin coating is the most widely used fabrication technique to produce perovskite thin films but is only suitable for small area substrates. The rotating motion of a spin coater causes higher velocity further away from the center of rotation as well as larger forces on the solution, which can result in nonuniform layer thickness for large samples. Furthermore, it produces a large amount of waste, as excess solution is needed for uniform coating. Conventional spin-coating of perovskite precursors in high boiling point solvents leads to perovskite formation with a branchlike morphology and poor surface coverage due to its low nucleation density and fast crystal growth upon annealing at 100 °C for several minutes.⁵ Significant improvement of the film quality of spin-coated perovskites was achieved by antisolvent techniques, introduced in 2014 by Jeon et al., who reached a certified world record PCE of 16.2% at that time.⁶ Other strategies to improve rapid and complete crystallization of perovskites include hot casting, gas flow drying and vacuum quenching.⁷−¹⁰ To make perovskite solar cells an industrially viable technology, scalable deposition methods are required. Among these, slot-die coating and blade coating have gained much attention during the last few years.¹¹−¹⁶

In slot-die coating, a precursor solution is dispensed in a controlled manner through a narrow slit onto a moving substrate, see Figure 1. Slot-die coating has several advantages over other deposition techniques: deposition is rapid, takes place on a well-controlled large area with a minimum of solution waste, and is compatible with continuous roll-to-roll processing. Thus, slot-die coating offers an outstanding platform to fabricate large-area thin films. Slot-die coating does not have the intrinsic drying mechanism occurring in the
spin-coating process and in many cases an air or nitrogen flow is used for slot-die coating of perovskites.\textsuperscript{17}

In 2015, Hwang et al. prepared perovskite solar cells by slot-die-coated PbI\textsubscript{2}, which was converted to MAPbI\textsubscript{3} perovskite either by dipping into MAI solution, or by slot-die coating of MAI solution. In combination with slot-die-coated ZnO and P3HT layers, they obtained maximum efficiencies of 11\% for both approaches.\textsuperscript{18} Cotella et al. obtained a maximum efficiency of 9.2\% from a single-step slot die deposition at 65 °C of perovskites on mesoporous titanium oxide using an airknife for improved film crystallization and uniformity.\textsuperscript{19} Similarly, Kim et al. used substrate heating (~60 °C) and nitrogen blowing for a single-step perovskite deposition to achieve power conversion efficiencies up to 12.7\%.\textsuperscript{20} For fully slot-die-coated devices (ZnO/perovskite/hole transport material (HTM), using a novel HTM, bifu-OMeTAD), Qin et al. obtained 14.7\%, compared to 8.4\% for spiro-OMeTAD.\textsuperscript{21} In 2018, Whitaker et al. obtained an efficiency of 18.0\% for slot-die-coated perovskite.\textsuperscript{22} They used a mixture of DMF and N-methyl-2-pyrrolidone (NMP) as precursor solvent; the deposition step was followed after 5 min by diethyl ether antisolvent dipping, N\textsubscript{2} drying, then preannealing at 50 °C and annealing at 140 °C under a petri dish. Dou et al. reported a PCE of 17.4\% for slot-die-coated MAPbI\textsubscript{3} from acetonitrile/methylamine solution at room temperature with only a brief heat treatment at 100 °C for 2 min.\textsuperscript{13}

In this work, we have developed a simple slot-die coating technique for lead halide perovskites on heated substrates with temperatures of about 90 °C under ambient conditions. By careful adjustment of deposition parameters, we obtained good quality MAPbI\textsubscript{3} perovskite films from which solar cells were prepared with a maximum PCE of 14.5\%, compared to 17\% for spin-coated MAPbI\textsubscript{3} films with antisolvent treatment. In the slot-die coating procedure, we simplified perovskite film deposition by avoiding additional treatments, such as antisolvent dropping or dipping, air blowing, or vapor annealing, which could be omitted when selecting proper deposition conditions. Interestingly, we could simply use dilutions of MAPbI\textsubscript{3} precursor formulations from spin-coating research. The slot-die coating process presented here can be considered to be a hot-coating method, which induces rapid perovskite crystallization. Such a method has been previously used in combination with spin-coating.\textsuperscript{7} We have used significantly higher substrate temperatures (~90 °C) than in other reports on slot-die coating of perovskites on heated substrates where temperatures of about 65 °C were used in combination with additional air or nitrogen flow.\textsuperscript{16,20}

\section*{EXPERIMENTAL SECTION}

The slot-die coater unit (Compact sheet coater, FOM technologies, Denmark) was placed in a fume hood; deposition took place in ambient air with a relative humidity of 40–50\%. In this system, the slot-die head is stationary while the hot plate carrying the substrates is moving. The speed was set to 150 cm min\textsuperscript{−1}, pump rate at 0.40 mL min\textsuperscript{−1}, and the slot width used was 2.8 cm. The measured temperature on the substrate surface was 70, 90, and 110 °C corresponding to a set temperature of 100, 130, and 150 °C on the slot-die coater. Substrates were warmed up on the hot plate for 15 min before coating. The coating solution was 0.45 M MAPbI\textsubscript{3} in DMF/DMSO (4:1 v/v). After deposition, substrates were left on the hot plate for a further 10 min at the same temperature before cooling down to 50 °C. The substrates were used conducting fluoride-doped tin oxide (FTO) glass (TEC15, 2.2 mm, Pilkington) with a dense layer of TiO\textsubscript{2} prepared by spray pyrolysis and further treated with aqueous TiCl\textsubscript{4} solution, followed by heating. Further experimental details are given in the Supporting Information.

\section*{RESULTS AND DISCUSSION}

Slot-die coating is one of the best methods to scale up solution-based thin film deposition. Figure 1 shows the schematics of the slot-die coating process. Slot-die coating is a noncontact technique in which solution is pumped from a syringe to the well-defined slit of a slot-die head unit at a defined pump rate (A in Figure 1). In the slot-die coater used here, the die head is fixed and the substrate is passed underneath at a set speed. The direction of substrate is indicated (B in Figure 1).

In this work, we mainly varied the substrate temperature to achieve good quality perovskite films. We applied significantly higher substrate temperatures compared to previous reports in order to facilitate good crystallization of the perovskite and complete evaporation of the solvents without further after treatments. Within a span of seconds after the solution was dispensed, a black dense perovskite film was formed, indicating both rapid crystallization of perovskite and rapid evaporation of the solvents. We selected three different substrate temperatures for slot-die coating, 70, 90, and 110 °C. At lower temperature (70 °C), the thin film was not fully converted into perovskite, as is evident from XRD analysis, see Figure S1 in Supporting Information. At higher temperature (110 °C) a larger amount of PbI\textsubscript{2} is found in the deposited films, most likely due to loss of MAI at higher temperatures. Under optimum conditions, substrates were heated to 90 °C. This resulted in direct formation of high quality MAPbI\textsubscript{3} perovskite thin films with a minimum amount of PbI\textsubscript{2}.

Uniform, pinhole free films can be made using slot-die coating when the deposition parameters are carefully controlled. A photograph of typical slot-die-coated MAPbI\textsubscript{3} perovskite films under optimal deposition conditions on large substrates (12 cm × 2.8 cm) is shown in Figure 2a. Viewed from an angle, the films look grayish; they do not have a specular reflection. This points to significant surface roughness. Viewed from the top or through the FTO substrate, the films look very dark brown to black, see Figure 2d. The SEM cross-section of the slot-die-coated perovskite (Figure 2b) shows that the film has large grains. An illustration of the solar cell device architecture used in this study is presented in Figure 2c, and photographs of the actual devices are shown in Figure 2d.

In slot-die coating, the film thickness is controlled by various factors such as the precursor concentration, pumping rate, and the substrate speed. Other important factors for obtaining high-quality films are the gap height between the slot-die head and substrate, wetting of the substrate by the solution, the substrate temperature, and the airflow over the wet film.\textsuperscript{22,23}

To optimize the concentration of precursor solution, we
Figure 2. (a) Photograph of slot-die-coated MAPbI₃ films. (b) SEM cross-section of a slot-die-coated MAPbI₃ film on FTO/TiO₂ substrate. (c) Device architecture. (d) Images of complete solar cells viewed from the top (left) and from the FTO side (right).

diluted the MAPbI₃ spin coating solution to 0.60, 0.50, 0.45, and 0.40 M. The optimal concentration to obtain a film thickness of 500 to 600 nm was 0.45 M, which is about 2.6 times lower than typical spin coating solutions for perovskite deposition. SEM cross sections of each concentration are shown in Supporting Information (Figure S2), along with a thickness versus concentration graph in Figure S3. We found that good perovskite films could be obtained by slot-die coating using precursor solutions that are similar to those used for spin coating but significantly diluted.

We adopted a slow cooling process for lead halide perovskite films on the glass-based substrates. Typically, the films were allowed to cool down from 90 to 50 °C during about 30 min. We found that more rapid cooling was detrimental to the performance of resulting solar cell devices. Thermal shock can lead to stress and defects in the deposited films. In many cases, we found that rapid cooling led to perovskite films that had a slight whitish color when viewed from the FTO side, see Figure S4 in SI. This could point to voids or partial delamination of the perovskite film from the TiO₂ layer. MAPbI₃ and glass have significantly different linear thermal expansion coefficients, namely, 1.3 × 10⁻⁴ and 8.6 × 10⁻⁴ K⁻¹, respectively. Cooling the MAPbI₃ perovskite film on a glass-based substrate by 70 °C causes the perovskite film to shrink by 1%, but the glass by less than 0.1%. Rapid cooling does not allow the perovskite film to relax, which will cause cracks, voids, or delamination of the film.

To investigate the film morphology of perovskite films in more detail, scanning electron microscopy (SEM) and optical microscopy analysis was carried out. We compared slot-die-coated films morphology with standard spin-coated MAPbI₃ films. Figure 3 shows the scanning electron microscope images of slot-die-coated films with a large grain size of 100–200 μm with a flowerlike morphology. The same structure is also visible with optical microscopy (Figure 3c). These are consistent with the film morphology reported for the hot-casting spin coating method reported by Nie et al. Sudden evaporation of the solvent from the casted solution on the heated substrate can lead to rapid growth of large perovskite grains up to a millimeter size. This kind of rather uncontrolled growth usually results in large flowerlike morphology, both in hot-casting spin-coating and in slot-die coating as found here. Higher-magnification SEM of slot-die-coated films reveal small hexagonal flakes on top of the MAPbI₃ film, see Figure S5 in Supporting Information. Possibly, these are PbI₂ crystals, which would be in accordance with XRD and HAXPES results (discussed below).

Figure 3b,d shows micrographs of MAPbI₃ perovskite thin films made using the spin-coating technique with antisolvent quenching. Very smooth and homogeneous films are obtained with average grain size of about 250 nm (see high-magnification SEM in SI Figure S6). The insets in Figure 3a,b show the roughness profiles of the different films as measured by profilometry (see Figure S7 in SI for an enlarged image). There is a very large difference in roughness between the two types of processing techniques. For slot-die-coated films, the roughness is up to 200 nm, while that of spin-coated films with antisolvent treatment is as low as 15 nm, both for perovskite films with a nominal thickness of 500 nm. The highest thickness peaks in the slot-die-coated films are located in the center of the large crystals, which are the initial seedling points for islandlike growth through a Volmer–Weber mechanism. The high roughness and thickness variations of slot-die-coated films are expected to be disadvantageous for solar cell devices.

The optical properties of both slot-die-coated and spin-coated films are shown in Figure 4, which shows the total and diffuse transmittance of the slot-die and spin-coated thin films. The spin-coated sample shows interference fringes in the nonabsorbing 800–1600 nm range, which is an indication of a homogeneous thickness and a flat surface of the perovskite film. Such fringes are not seen in the rougher slot-die-coated thin films. The diffuse transmission contribution is higher in the slot-die-coated thin film, reaching 22% compared to 17% maximum for spin-coated film. The absorbance in Figure 4b shows a rather similar behavior from the two thin films with a band gap absorption at approximately 1.60 eV (767 nm). The absorbance above 800 nm is a contribution mainly from the FTO substrate (light absorption by conduction band electrons); reflectance spectra are presented in SI, Figure S8.

Figure 5a shows the steady-state photoluminescence (PL) spectra of slot-die-coated and spin-coated films on Al₂O₃-coated glass. The PL intensity of spin-coated MAPbI₃ films is much higher than that of slot-die-coated films by a factor of 8.
The PL peak position and width are identical (see SI Figure S9 for normalized spectra). The lower PL of slot-die-coated films is indicative of rapid nonradiative recombination processes, which could be caused by defects, located either in the bulk or at the surface of the perovskite. The relatively high temperature annealing for almost 10 min could be the origin of formation of such defects in slot-die-coated films. Specifically, MAI could leave the MAPbI3 in the form of gas-phase methylamine and hydroiodic acid, resulting in iodide and methylammonium vacancies. It was reported by Conings et al. that prolonged heating to 85 °C resulted in a decrease of PL for MAPbI3 films, even in inert gas atmospheres.26

Figure 5b shows the X-ray diffraction pattern of slot-die-coated and spin-coated films. The PL peak position and width are identical (see SI Figure S9 for normalized spectra). The lower PL of slot-die-coated films is indicative of rapid nonradiative recombination processes, which could be caused by defects, located either in the bulk or at the surface of the perovskite. The relatively high temperature annealing for almost 10 min could be the origin of formation of such defects in slot-die-coated films. Specifically, MAI could leave the MAPbI3 in the form of gas-phase methylamine and hydroiodic acid, resulting in iodide and methylammonium vacancies. It was reported by Conings et al. that prolonged heating to 85 °C resulted in a decrease of PL for MAPbI3 films, even in inert gas atmospheres.26

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Figure 5b shows the X-ray diffraction pattern of slot-die-coated and spin-coated films on Al2O3 coated glass substrate. (b) X-ray diffraction patterns of slot-die-coated and spin-coated films. Two different emission angles (angle between the detected electron and surface normal) were used 62° and 12° to analyze the films, giving an estimated
probing depth of 8.8 and 18.4 nm, respectively. In the survey spectra (Figure S11 in SI) no core levels specific for the substrate, that is, Ti 2p from Ti, could be observed, supporting the conclusion that the films are pinhole free. Moreover, the O 1s signal from both samples was very low and similar in intensity; there is no indication for the formation of lead oxide, see Figure S11 and Table S1 in SI.

The HAXPES Pb 4f, I 4d, and N 1s core level spectra, normalized with respect to the area of the Pb 4f core level, are shown in Figure 6. The slot-die-coated MAPbI₃ film shows a lower iodine to lead ratio and a significantly lower nitrogen to lead ratio compared to the spin-coated film. As the origin of N in the HAXPES spectra is from methylammonium in the sample, this suggests a loss of MAI in slot-die-coated film compared to the spin-coated film and an enrichment in PbI₂. Details of the elemental ratios estimated from HAXPES are provided in the Supporting Information in Table S1. From the estimated atomic ratios, it can be concluded that about half of the methylammonium is missing at the surface (∼10 nm) of the slot-die-coated films, while no depletion is found for the spin-coated films. MAI can escape during the heat-assisted fabrication technique in the form of methylamine and hydroiodic acid gases, explaining this difference.

Comparing the two emission angles, the more surface sensitive measurement shows lower values of iodine and nitrogen relative to lead for the slot-die-coated films, indicative that MAI-loss is indeed a surface-related reaction. In the Supporting Information, we validate the accuracy of this conclusion considering the relatively high roughness of the slot-die-coated film (see comment S1 in Supporting Information).

The substrate plays an important role in the slot-die coating process. It must provide good wettability with the precursor solution in order to obtain high quality films. In this study, we chose titanium tetrachloride (TiCl₄) treated compact TiO₂ on FTO glass as the substrate, providing the electron selective contact for the perovskite solar cell. Compact TiO₂ films prepared by spray pyrolysis were found to be unsuitable as substrates for slot-die coating of perovskite under the conditions used here, as these gave highly variable and rather poor results. Specifically, there were problems with the wetting of these films during the slot-die deposition and with adherence of the perovskite films. Sometimes a whitish color was observed when facing from the glass side, see Supporting Information Figure S4. The white appearance is probably due to an optical effect due to a loss of adherence or cracks between TiO₂ and perovskite layer. Such cracks can be formed upon fast cooling given the large difference in expansion coefficients of the two materials (TiO₂ on glass and perovskite).

We selected aqueous titanium tetrachloride treatment as a way to improve the TiO₂ contact. TiCl₄ treatment improved the wetting with the perovskite precursor solution and led to better and more reproducible solar cell performance compared to untreated TiO₂ substrates. With longer TiCl₄ treatment of the substrates, there was less probability of cracks and whitish color at the interface. Both a slow cooling down process and the time duration of TiCl₄ affected the interface and in the end the solar cell performance. The effect of time duration for TiCl₄ treatment on PCE is shown in SI Figure S13a and UV–visible spectra of MAPbI₃ films on different time treated TiCl₄ substrate in Figure S13b.

Despite the rather high roughness of the slot-die-coated films, we were able to make efficient solar cell devices using production steps identical to those used to make devices from spin-coated films except for the perovskite deposition. The J–V curves of the best performing devices from spin-coating and slot-die coating are shown in Figure 7a, yielding an efficiency of 17% for spin-coated and 14.5% for slot-die-coated solar cells. The TiCl₄ treatment time was 50 min and substrate temperature for slot-die coating was 90 °C. Details of all parameters are shown in SI Table S2. Figure 7b shows the PCE statistics of spin-coated (n = 40) and slot-die-coated (n = 60) solar cell devices. Only the perovskite layer was prepared by spin-coating and slot-die coating, respectively, the other fabrication steps were identical. An average efficiency of 12.0% was obtained for slot-die-coated devices, compared to 15.7% for spin-coated devices. The lower performance of slot-die-coated devices is due to slightly lower short-circuit photocurrent densities (Jₜₚ) and significantly lower fill factors (FF), see Figure S14 in SI. Interestingly, very high values for the open-circuit potential (Vₜₚ) were obtained, more than 1.0 V, which was higher than that found for the spin-coated devices. A possible origin for these differences is that a relatively thick spiro-MeOTAD layer may be formed on the rougher slot-die perovskite film (the spin-coating conditions for the spiro were not adjusted), leading to additional internal resistance, giving poor fill factors. Alternatively, some contact loss may occur between perovskite and TiO₂, leading to lower Jₜₚ and FF. The high Vₜₚ points to the good quality of the slot-die deposited MAPbI₃.

Hysteresis in the current–voltage characteristics of perovskite solar cells is commonly observed. Typically, it is more pronounced in PSC devices with only a compact TiO₂ layer as electron-selective contact, compared to those that have an additional mesoporous TiO₂ layer. Here, we found significant hysteresis in all devices; it was found to be larger in the devices with slot-die-coated perovskite films compared those with the spin-coated films. See Figure S15 in SI for J–V curves for slot-die-coated and spin-coated film. The interfacial contact between TiO₂ and perovskite has significant importance; a partial contact loss can give rise to hysteresis. In the case of large perovskite grains, as in the slot-die-coated devices, the risk of partial delamination from the TiO₂ blocking layer is higher than with spin-coated films, having smaller grains.

In additional studies, we included maximum power point (MPP) tracking for testing the slot-die-coated perovskite solar cell devices, see Supporting Information Figure S15. The PCE...
during MPP tracking was considerably lower than that that derived from J–V-curves (7% vs 13% in initial J–V curves). This suggests that there is a problem at the interfaces between the perovskite and the selective contacts. At the hole-selective contact, the high roughness of the perovskite layer and/or the observed MAI deficiency could cause problems. At the electron-selective contact, there could be problems as a result of the temperature changes in the synthesis process, which can cause poor contact. Further work is needed to resolve these issues.

The substrate temperatures during perovskite slot-die coating is critically dependent for the solar cell performance: devices prepared at 70 and 110 °C gave significantly lower efficiencies of 5.3% and 11.3%, respectively, from J–V curves. The low efficiency at 70 °C might be due to incomplete conversion to the perovskite structure. At higher substrate temperatures (110 °C), we have more loss of MAI, which is indirectly seen in the XRD with the higher PbI₂ peak. This is one of the plausible reasons for the lower performance.

**CONCLUDING REMARKS**

Highly crystalline methylammonium lead iodide perovskite films were deposited using slot-die coating with diluted precursor solutions from spin-coating. Deposition on a hot substrate (90 °C) provides immediate formation of a dense black crystalline perovskite film without the need for antisolvent or other after-treatments. Such hot casting of the high-boiling point precursor solutions leads to films with large perovskite crystals, but it has the disadvantage of giving high roughness in the resulting films. Despite the high roughness (200 nm for 500 nm thick films), we were able to make efficient solar cell devices, reaching up to 14.5%, using production steps identical to those used to make devices from spin-coated films.

The slot-die coating procedure for MAPbI₃ thin films described here can definitely be further optimized. Some suggestions are given here: A slight excess of MAI in precursor solution could compensate for the observed MAI loss; Liao et al. demonstrated in recent work that a 5% MAI excess in a hot-casting process yielded highly crystalline perovskite films with complete conversion of PbI₂ to perovskite and best solar cell performance.³⁴ Alternatively, one can change to more thermally stable perovskites, such as formamidinium lead halides. These perovskites can withstand high temperatures compared to perovskites with methylammonium.³⁵,³⁶ Finally, lowering the deposition temperature could improve the efficiency of perovskite solar cells, but this would require a change of the current solvent system, which needs a minimum substrate temperature of 90 °C for the complete conversion of perovskite. By changing the solvent ratios and solvents, one can achieve lower temperatures for successful lead halide perovskite deposition.

**ASSOCIATED CONTENT**

- **Supporting Information**
  
  The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaeem.0c00039.

  Experimental details; X-ray diffraction patterns of slot-die-coated MAPbI₃ films formed at different substrate temperatures; SEM cross section of MAPbI₃ films prepared from different molar precursor solution; thickness of the slot-die-coated MAPbI₃ film versus the concentration of the precursor solution; images of slot-die-coated MAPbI₃ solar cells viewed from the glass side; higher-magnification SEM of slot-die-coated MAPbI₃ films; roughness profiles for slot-die-coated and spin-coated film; reflection spectra of slot-die-coated and spin-coated MAPbI₃ films; normalized photoluminescence spectra of spin-coated and slot-die-coated MAPbI₃ films; derivative of the surface roughness; HAXPES spectra of slot-die-coated and spin-coated films; estimation the relative concentrations of the elements from HAXPES analysis; schematic description of the incident photon beam and the electrons emitted in the direction of the spectrometer; optimized parameters for MAPbI₃ slot-die coating in this study, box charts for PCE of different duration of TiCl₄; UV-visible spectra of MAPbI₃ films on different time treated TiCl₄ substrates; statistics of the photovoltaic characteristics of slot-die-coated and spin-coated cells (PDF)

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**Notes**

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**REFERENCES**

(1) Tuller, H. L. Solar to Fuels Conversion Technologies: A Perspective. Mater. Renew. Sustain. Energy 2017, 6 (1), 3.
et al. Roll-to-Roll Printing of Perovskite Solar Cells. L. M.; Ryter, J.; Breslin, N. J.; Berry, J. J.; Garner, S. M.; Barnes, F. S.; 2018 on 6-in. Substrate Using Slot Die Coating. Production of High Efficiency Perovskite Module and Solar Cells of Flexible Perovskite Solar Cells in Ambient Conditions. Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. Energy Environ. Mater. Deposition Methods for Large-area Production of Perovskite Thin Films. Energy Environ. Mater. www.acsaem.org of Perovskite Thin-Film Solar Cells. Angew. Chem. 2014, 126 (37), 10056–10061. Solvent Engineering for High-Performance Inorganic–Organic Hybrid Perovskite Solar Cells. Nat. Mater. 2014, 13, 897. Nie, W.; Tsai, H.; Asadpour, R.; Blancou, J.-C.; Neukirch, A. J.; Gupta, G.; Crochet, J. J.; Chhowalla, M.; Tretiak, S.; Alam, M. A.; Wang, H.-L.; Mohite, A. D.; et al. High-Efficiency Solution-Processed Perovskite Solar Cells with Millimeter-Scale Grains. Science (Washington, DC, U.S.) 2015, 347 (6221), 522–525. Su, J.; Cai, H.; Ye, X.; Zhou, X.; Yang, J.; Wang, D.; Ni, J.; Li, J.; Zhang, J. Efficient Perovskite Solar Cells Prepared by Hot Air Blowing to Ultrasonic Spraying in Ambient Air. ACS Appl. Mater. Interfaces 2019, 11 (1), 10689–10696. Ding, B.; Li, Y.; Huang, S.-Y.; Chu, Q.-Q.; Li, C.-X.; Li, C.-J.; Yang, G.-J. Material Nucleation/Growth Competition Tuning towards Highly Reproducible Planar Perovskite Solar Cells with Efficiency Exceeding 20%. J. Mater. Chem. A 2017, 5 (15), 6840–6848. Gao, L.-L.; Li, C.-X.; Li, C.-J.; Yang, G.-J. Large-Area High-Efficiency Perovskite Solar Cells Based on Perovskite Films Dried by the Multi-Flow Air Knife Method in Ambient Air. J. Mater. Chem. A 2017, 5 (4), 1548–1557. Hwang, K.; Jung, Y. S.; Heo, Y. J.; Scholes, F. H.; Watkins, S. E.; Subbiah, J.; Jones, D. J.; Kim, D. Y.; Vak, D. Toward Large Scale Roll-to-Roll Production of Fully Printed Perovskite Solar Cells. Adv. Mater. 2015, 27 (7), 1241–1247. Di Giacomo, F.; Shanmugam, S.; Felderres, H.; Bruijaers, B. J.; Verhees, W. J. H.; Doreen Kamper, M. S.; Veenstra, S. C.; Qiu, W.; Gehlhaar, R.; Merekas, T.; et al. Up-Scale Sheet-to-Sheet Production of High Efficiency Perovskite Module and Solar Cells on 6-in. Substrate Using Slot Die Coating. Sol. Energy Mater. Sol. Cells 2018, 181, 53. (19) Cotella, G.; Baker, J.; Worsley, D.; De Rossi, F.; Pleydell-Pearce, C.; Carnie, M.; Watson, T. One-Step Deposition by Slot-Die Coating of Mixed Lead Halide Perovskite for Photovoltaic Applications. Sol. Energy Mater. Sol. Cells 2017, 159, 362–369. (20) Kim, J. E.; Jung, Y. S.; Heo, Y. J.; Hwang, K.; Qin, T. S.; Kim, D. Y.; Vak, D. Slot Die Coated Planar Perovskite Solar Cells via Blowing and Heating Assisted One Step Deposition. Sol. Energy Mater. Sol. Cells 2018, 179, 80–86. (21) Qin, T. S.; Huang, W. C.; Kim, J. E.; Vak, D. J.; Forsyth, C.; McNeill, C. R.; Cheng, Y. B. Amorphous Hole-Transporting Layer in Slot-Die Coated Perovskite Solar Cells. Nano Energy 2017, 31, 210–217. (22) Whittaker, J. B.; Kim, D. H.; Larson, B. W.; Zhang, F.; Berry, J. J.; van Hest, M. F. A. M.; Zhu, K. Scalable Slot-Die Coating of High Performance Perovskite Solar Cells. Sustain. Energy Fuels 2018, 2 (11), 2442–2449. (23) Krebs, F. C. Sol. Energy Mater. Sol. Cells 2009, 93, 394–412. (24) Jacobsson, T. J.; Schwab, L. J.; Ottosson, M.; Hagfeldt, A.; Edvinsson, T. Determination of Thermal Expansion Coefficients and Locating the Temperature-Induced Phase Transition in Methylammonium Lead Perovskites Using X-Ray Diffraction. Inorg. Chem. 2015, 54 (22), 10678–10685. (25) Zheng, Y. C.; Yang, S.; Chen, X.; Chen, Y.; Hou, Y.; Yang, H. G. Thermal-Induced Volmer–Weber Growth Behavior for Planar Heterojunction Perovskite Solar Cells. Chem. Mater. 2015, 27 (14), 5116–5121. (26) Conings, B.; Drijkoningen, J.; Gautquelin, N.; Babayigit, A.; D’Haen, J.; D’Olieslaeger, L.; Ethirajan, A.; Verbeek, J.; Manca, J.; Mosconi, E.; Angelis, F. D.; Boyen, H.-G.; et al. Intrinsic Thermal Instability of Methylammonium Lead Trihalide Perovskite. Adv. Energy Mater. 2015, 5 (15), 1500477. (27) Szafranski, M.; Katuriak, A. Mechanism of Pressure-Induced Phase Transitions, Amorphization, and Absorption-Edge Shift in Photovoltaic Methylammonium Lead Iodide. J. Phys. Chem. Lett. 2016, 7 (17), 3458–3466. (28) Ma, Y.; Hangoma, P. M.; Park, W. I.; Lim, J.-H.; Jung, Y. K.; Jeong, J. H.; Park, S. H.; Kim, K. H. Controlled Crystal Facet of MAPbI3 Perovskite for Highly Efficient and Stable Solar Cell via Nucleation Mediation. Nanoscale 2019, 11 (1), 170–177. (29) Muscarella, L. A.; Hutter, E. M.; Sanchez, S.; Dieleman, C. D.; Savenije, T. J.; Hagfeldt, A.; Saliba, M.; Ehrler, B. Crystal Orientation and Grain Size: Do They Determine Optoelectronic Properties of MAPbI3 Perovskite? J. Phys. Chem. Lett. 2019, 10 (20), 6010–6018. (30) Zheng, Z.; Liu, A.; Wang, S.; Wang, Y.; Li, Z.; Lai, W.; Zhang, L. In Situ Growth of Epitaxial Lead Iodide Films Composed of Hexagonal Single Crystals. J. Mater. Chem. 2005, 15 (42), 4555–4559. (31) Ostapchenko, V.; Huang, Q.; Zhang, Q.; Zhao, C. Effect of TiCl4 Treatment on Different TiO2 Blocking Layer Deposition Methods. Int. J. Electrochem. Sci. 2017, 12 (3), 2262–2271. (32) Snaith, H. J.; Abate, A.; Ball, J. M.; Eperon, G. E.; Leijtens, T.; Noel, N. K.; Stranks, S. D.; Wang, J. T.-W.; Wojciechowski, K.; Zhang, W. Anomalous Hysteresis in Perovskite Solar Cells. J. Phys. Chem. Lett. 2014, 5 (9), 1511–1515. (33) Unger, E. L.; Hoke, E. T.; Bale, C. D.; Nguyen, W. H.; Bowring, A. R.; Heumüller, T.; Christoforo, M. G.; McGhee, M. D. Hysteresis and Transient Behavior in Current–Voltage Measurements of Hybrid-Perovskite Absorber Solar Cells. Energy Environ. Sci. 2014, 7 (11), 3690–3698. (34) Liao, K.; Yang, J.; Li, C.; Li, T.; Hao, F. Off-Colorimetric Methylammonium Iodide Passivated Large-Grain Perovskite Film in Ambient Air for Efficient Inverted Solar Cells. ACS Appl. Mater. Interfaces 2019, 11 (43), 39882–39899. (35) Binek, A.; Hanusch, F. C.; Docampo, P.; Bein, T. Stabilization of the Trigonal High-Temperature Phase of Formamidinium Lead Iodide. J. Phys. Chem. Lett. 2015, 6 (7), 1249–1253. (36) Wang, M. Exploring Stability of Formamidinium Lead Trilalide for Solar Cell Application. Sci. Bull. 2017, 62 (4), 249–255.