3D Printer Based Slot-Die Coater as a Lab-to-Fab Translation Tool for Solution-Processed Solar Cells

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Solution-processed solar cells continue to show great promise as a disruptive energy generation technology due to their inherently low manufacturing costs and increasing efficiencies.[1–3] In this communication, we report the use of a 3D printer platform as a fabrication tool for solution-processed solar cells. This scalable, easily transferable coating process was used to make devices of different sizes and structures toward the aim of advancing the large-scale development of solution-processed solar cells. Organic bulk heterojunction (BHJ) and perovskite-based devices are both examples of solution-processed solar cells that can be made at low temperature, from solution and onto flexible substrates. Recent advances in material and device structure development have seen lab-scale device power conversion efficiencies (PCEs) approach those of more established solar technologies. For BHJ devices, the highest power conversion efficiency reported in the open, peer-reviewed literature is over 9%4 while a value of 11.1% has been reported for a device based on an undisclosed structure.[5] The earliest reports of organolead halide perovskite-based solar cells used a dye sensitized solar cell (DSSC) configuration which requires a sintered TiO₂ particle layer.[6,7] The PCE of devices using mesoporous-based structures have been rapidly increasing. A record efficiency of 19.3% has been reported very recently.[8] Perovskite-based devices without mesoporous TiO₂ structure have also been developed recently. It is reported that over 15% PCE can be achieved via a low temperature, solution-based process.[9]

Despite these advances in headline PCEs, the highest reported efficiency for fully printed BHJ devices has been steady[10,11] and no printed perovskite solar cells via roll-to-roll compatible process have been reported to date. The primary reason for this is that printing facilities are not readily accessible to most researchers. Therefore, most research groups report the performances of devices fabricated by spin coating on small substrates and still claim that the process or material will be useful in large-scale production in the future. However, the dynamics of solutions in the spin coating process are quite different from those of scalable coating processes. In addition, roll-to-roll processes typically require larger amounts of materials than are commonly used in research labs. We have used an industrial printer to produce BHJ solar cells[12] and found that over 30 L of ink was required to start roll-to-roll production. On a smaller scale, an industrial proofer, which is used to mimic printing conditions in a roll-to-roll production line, still consumed a lot of ink, with 100 mL of ink and 3 g of polymer typically used in a single set of experiments.[12] Even a small, laboratory scale, roll-to-roll printer typically requires a few tens of milliliters of ink. Although most of the ink used to fill the reservoir can often be recovered, the amount of material required to test various formulations is far more than typically available for newly synthesized materials. Therefore, very few results for fully printed solar cells have been reported with high performance materials.

The convergence of BHJ, DSSC, and perovskite device structures provides the field with an opportunity to now focus on the “lab-to-fab” translation of these solar cell technologies. To do this, ready access to a coating process that enables the solution-based deposition of multiple layers is required. In the general area of rapid prototyping, 3D printing has emerged as a powerful tool for the low-cost, rapid production of industrial products or prototypes.[13] 3D Printing is an example of additive manufacturing that builds a device from a surface, directly from a design meaning that a computer-aided design (CAD) file can be transformed to a finished product without additional cutting or assembling steps. Among the many types of 3D printers that are available, the fused deposition modeling (FDM) type printer has been developed rapidly and is becoming more and more popular as it becomes more affordable. FDM 3D printers have been developed to produce objects by printing multiple thick layers (typically over 100 µm) of melted plastic but can also be used to produce thin, solid films. FDM 3D printers are technically an automated extruder with x, y, z position control and typically can vary head speed/acceleration/deceleration as well as the temperature of the nozzles and a printing bed. Resources to build and control FDM 3D printers have been developed and shared by an open source community.[14] We therefore recognized that such a printer could be used as a comprehensive research tool kit if converted to allow processing of solutions instead of solid filaments. Furthermore, we also recognized that 3D printers have a number of other advantages over conventional printers/coaters. As a 3D printer is controlled by digital code, no hardware change is required to vary the printing pattern, allowing different device structures or designs to be tested without preparing new masks, forms, or other physical patterning. The digital instruction protocol, G code, is a machine-independent standard which means that optimized printing conditions can be transferred from machine.
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Supporting Information). The print head could thus be used for both printing parts and solar cells. During initial trials we found several shortcomings in our first head design. These problems could be instantly rectified by modifying the initial design, printing the design file, and replacing the original part. This iterative process could consume a lot of development time with conventional manufacturing methods. By contrast, with a 3D printer, the time required for the production of new parts is significantly reduced.

Figure 1b shows a printed, patterned poly(3-hexylthiophene) (P3HT) film applied by the modified printer with a point nozzle (a blunt needle). P3HT, a common polymer in OPVs, was used due to its ready availability. To produce an image pattern, an industrial standard STL file was prepared by CAD software. The STL file was converted to G code by software called a slicer and printed using standard 3D printing conditions. Relative thickness could be controlled by changing setting values in the slicer software. The figure clearly shows the advantages of digital printing—any pattern can be printed without changing the hardware. For rapid processing, we developed a script which converts all printing parameters to G code. Parameters used to control the printer can be seen in Figure S2, Supporting Information. An electrode pattern for solar cell modules, shown in Figure 1b, was prepared simply by setting the gap of each subcell, the width of the busbar and the grid interval. Both images were printed in one printing run by pasting two sets of G code into the printing software. Potentially, this approach could be useful for multiple heads, which are common in 3D printers. Multilayer structures can be developed individually and all code can be integrated for the fabrication of a completed solar cell in one printing run. A link to a movie of the printing process can be found in the Supporting Information.

Although the point nozzle can produce any pattern, it is not ideal for making the thin and uniform coatings required in solar cells. Therefore, a mini slot-die head was also prepared. The slot-die head was designed to be used with metal shims which determine the coating width. An additional meniscus guide, developed for a well-defined coating pattern, was also adopted as shown in Figure S1, Supporting Information. To ensure compatibility with organic solvents the slot-die head was made from stainless steel in a conventional metal workshop. Slot-die coating is a 1D coating method that typically produces a continuous stripe with a defined width and uniform thickness over a large area can be typically obtained. We refer to the printer with the slot-die head as a “3D coater” by contrast with the 3D printer with the point nozzle. Figure 1c shows 13 mm stripes prepared in coating mode. High quality, uniform coating over 100 mm lengths could be obtained. However, the end of each print was always thicker due to a lift-off pattern. Unlike conventional slot-die coating, curved stripes could be also prepared, as shown in the figure. This demonstrates another advantage of the 3D printing platform—solar cells with nonconventional designs can be fabricated.

To fabricate BHJ solar cells with the printer, we first fabricated small, laboratory scale devices on 25 × 25 mm² ITO-glass. An issue we encountered when printing a photoactive layer on such small substrates was reliability. Printing was carried out in the following sequence: (i) the nozzle dispenses a few µl of ink to fill the void in the nozzle and to wet the end of the nozzle
Contact, dispense a small amount of ink (≈1–5 µL) to form the meniscus and then lift up to coating height. By introducing this additional step, reliability was greatly improved. The idea could be realized by simple script editing instead of re-engineering the whole printer, which might be necessary for conventional equipment. This example clearly shows the advantages of a 3D printer as a research tool. New ideas can be quickly applied in the process. After solving the reliability issue, BHJ devices were fabricated on 25 × 25 mm² ITO-glass substrates. To account for lift-off patterns, coating was extended to an adjacent substrate (making the coating length 30 mm) to leave the lift-off pattern outside of the device substrate.

To fabricate BHJ device with the process, we first confirmed device performance with well-studied P3HT device. We were able to make devices with comparable performance to our typical spin-coated device as shown in Figure S4, Supporting Information. After confirming a working BHJ solar cell made using the 3D coater, devices based on an alternative polymer were explored to achieve high performance. Poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′benzothiadiazole)] (PCDTBT) is a widely available polymer that has been used for high performance devices (>7% PCE).[16–19] shown high thermal stability[20] and devices with long operational lifetimes.[21] Unlike P3HT, low-band-gap polymers such as PCDTBT typically show low tolerance to thickness variation, with the best performance in a narrow thickness range of only ≈70–100 nm.[22] To achieve this thickness, we used a relatively low concentration as lower concentration provides finer thickness control. Dichlorobenzene (DCB) solutions were prepared containing 10 mg of PCDTBT and 35 mg of [6,6]-phenyl-C70-butyric acid methyl-ester (PC70BM) in 3 mL of solvent (15 mg of solid in 1 mL of solution).

Slot-die is classified as a premetered coating[11] which means thickness is determined by the mass flow in the coating system. For a given coating speed and coating width, film thickness is determined by the amount of solution feed, as slot-die has no loss of ink in the coating process. However, we found, that for small devices, our system works more like self-metered coating, which means the thickness is determined by the coating conditions instead of the amount of solution flow. Dip coating, bar coating, and knife coating are also classified in this category. The reason for this difference in behavior was the short coating length and small material consumption. The ink required to wet the end of the nozzle and to form a meniscus was enough to form a ≈200 nm film on the small substrate. As a result, a uniform thin film 50–200 nm, which is the typical thickness range of photoactive layers, could not be prepared by controlling the amount of solution flow. Therefore, we used coating speed to fabricate devices with various thicknesses at a constant solution feed of 1 µL cm⁻². By varying the coating speed while maintaining a constant solution flow we were able to achieve control over film thickness in the required range as shown Figure 2b.

OPV devices based on PCDTBT were prepared using various coating speeds with a constant solution flow to calibrate coating conditions. In this way, 20–500 nm thick films could be fabricated from a single solution as shown in Figure 2b. However, we found poor uniformity with films that were over 200 nm in thickness. It was observed that uniform wet films lost their
uniformity during drying to thick films. Films under 200 nm in thickness showed reasonable uniformity as shown in Figure S3, Supporting Information. As we deliberately used low concentration for fine thickness control in ≈70–100 nm range, thicker uniform films can be prepared simply by using higher concentration. Two sets of films made using different coating speeds were fabricated in a random order to avoid any effects of gradual change of the system or solution. Within a batch, we found that the same coating speed reproducibly gave the same thickness films as shown in the figure. As discussed previously, the coater works like a self-metered coating method and the thicknesses of the films follow the power law of coating speed \( h = S^{0.61} \), which is close to that reported previously, ≈0.66.[23] Therefore, the thickness of films could be controlled easily after calibration as shown in Figure 2b and devices with active layer thicknesses varying across a desired range could be fabricated. It is a noteworthy feature of the coater that consumption of solution per device is only ≈5–10 µL, which includes the excess to wet the nozzle to form the meniscus. About ≈200–400 devices could be produced with 3 mL of the solution. This is more than an order of magnitude more efficient, with respect to solution consumption, than spin coating.

To investigate thickness-dependent device performance, inverted devices with a configuration ITO/ZnO/PCDTBT:PC71BM/MoO 3 /Ag were fabricated using a 3D-coated photoactive layer. The reason for choosing an inverted geometry was to fabricate fully printed devices once the application conditions were optimized. To date, no fully printed device with a conventional geometry has been successfully made with a roll-to-roll printing processes. The device performance trend for the inverted device, as a function of the coating speed of a batch, is illustrated in Figure 3a along with the optically measured thicknesses of the devices. The high molecular weight polymer was not completely soluble and the solid content of each solution varied slightly after filtration. This led to some batch-to-batch variation in thickness. Therefore, we measured the actual thickness of the photoactive layer of each device by optical methods, the results of which can be seen in the Supporting Information, instead of solely relying on the calibration curve in Figure 2b. At the lowest coating speed, 1 mm s \(^{-1} \), the device showed about 5.3% PCE with a FF of ≈63%. This is a surprisingly high efficiency as the photoactive layer is only 50 nm thick. The result demonstrates that this coating method can enable defect-free, thin films. The best device performance was obtained from an ≈70 nm thick photoactive layer, which is consistent with what has been reported in the literature.[22] Using the optimized coating conditions a PCE of over 6% PCE was obtained, which, based on a recent review article on roll-to-roll processed solar cells,[21] is the highest PCE so far obtained from a roll-to-roll compatible process. To confirm the high efficiency, the best coating condition, 3 mm s \(^{-1} \), was used to fabricate more devices. The PCE results for 36 devices fabricated using the same conditions from multiple batches are shown in the inset of Figure 3a. Although there were some inferior devices, most showed efficiencies over 6%. The best device showed PCE = 6.72%, Voc = 0.90 V, Jsc = 12.4 mA cm \(^{-2} \) and FF = 60.1%. This efficiency is comparable to that of optimized spin-coated devices reported in the literature.[22] With further increases in film thickness, efficiency rapidly dropped due to a lower FF, while the Voc was almost constant and only a small change was evident in the Jsc. The trends can be seen in Figure 3b as well as in the J–V curves in Figure 3c. The J–V curves for 2, 4, and 20 mm s \(^{-1} \) coating speeds were omitted for clarity.
made to get a reliable contact. Each layer was printed with a
ZnO coating speeds can be seen in Figure S5, Supporting
Information. Accordingly, we simply chose the middle coating
speed (2 mm s⁻¹) for our testing conditions.

To fabricate the active layer, the coating conditions optimized
for small devices were initially transferred without any modifi-
tion to the large-area devices. Initial trials based on conditions
that gave an active layer thickness of around 70 nm showed that,
over an active area of ≈50 cm² some defects were present. These
resulted in shorts that limited the performance of the devices.
To address this, we modified the printing conditions slightly to
give an active layer thickness of about 100 nm, a change that
is easily achieved with the 3D printer. As the film is thicker,
there is less chance of forming defects such as pinholes. The
J–V curve of the module is shown in Figure 4b. The module
showed PCE = 4.56%, Voc = 4.35 V, Jsc = 10.2 mA cm⁻², and
FF = 51.1%. The best small device fabricated from the same
solution and the same coating conditions showed PCE = 5.18%,
Voc = 0.88 V, Jsc = 10.66 mA cm⁻², and FF = 55.2%. To com-
pare the module efficiency with the small size device, the J–V
curve of the small-size device is also shown in Figure 4b. As the
small-size device is a single cell, we also added a J–V curve of
a simulated module based on the small-size device. The curve
was made by simply multiplying by five, as the module consists
of five cells in series connection. If five small cells with same
performance are fabricated and perfectly connected in series
without any defect, the J–V curve would match the simulated
curve. Surprisingly, the module with about 500 times larger
active area than the small device showed comparable perform-
ance to that of the simulated module. The translational effi-
ciency in going from a tiny cell to a large module is therefore
high. The PCE of the large module is about 88% of that of
0.1 cm² small size device and the Voc is about same as fi ve times
the Voc of a single cell. The results confi rm that a high-quality
fi lm was formed over the larger area without defects. Based on
a recent review,[24] this is the highest PCE for a solution-pro-
cessed OPV module reported in the peer-reviewed literature to
date. As the previous record was for a spin-coated module on
a small substrate with only 0.6 cm² active area,[25] our result is
a significant advance. More importantly, the high-performance
module could be fabricated easily; a longer coating length and
more coating stripes in the printing input form of the control
software were all that were required to fabricate this module.
In addition to the large scale module, we were able to demon-
strate fabrication of fully printed device by using printing mode
to print silver grid electrode as shown in Figure S6, Supporting
Information. The easy and affordable way to test new materials
in a printing environment will therefore be extremely useful to
make progress towards roll-to-roll production of printed solar
cells.

As noted previously, devices based on PCDTBT require pre-
cise control of a ≈70–80 nm fi lm thickness. This is a challenge
for large-scale deposition and can be addressed by developing
a coating method with an appropriate tolerance or by devel-
oping a new ink that is optimized for thicker devices. As both
options are challenging, the literature has few examples of effi-
cient, large-scale devices with such low bandgap polymers. We
chose the fi rst option to demonstrate an effi cient, large-scale
device. To fabricate a large-area device, we adopted a conven-
tional, series-connected-module design as shown in Figure 4a.
ITO strips (13 mm wide with 2 mm gaps) were patterned on
to glass substrates. Extended ITO patterns at both ends were
made to get a reliable contact. Each layer was printed with a
small offset (=0.5 mm) to make the series connection. As the
offset can vary in each sample, the active area of the device,
which is defi ned by where ITO and metal electrode overlap,
for each sample was manually measured. To produce mod-
ules, the ZnO layer was printed fi rst. The solution used in spin
coating was used without dilution. When testing small devices
with 3D-coated ZnO layers, we found that variation of the ZnO
solution coating conditions has little or no effect on the per-
formance of the device. The performance trend with different

Figure 4. a) Schematic drawing of a module with 5 cells in series connec-
tion on a 10 × 10 cm² substrate. b) J–V curve of a module with 47.3 cm²
of active area and a single cell with 0.1 cm² of active area. Both devices
were fabricated at same coating condition.
converted to \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) by a dipping process. Printing the \( \text{PbI}_2 \) layer by the slot-die coating was more challenging than printing polymers. Firstly, the thickness required for perovskite solar cells (=300–500 nm) is much thicker than BHJ solar cells (=100–200 nm). Therefore, a significantly thicker wet film had to be prepared. As was the case for the polymer films, the process of drying thick, wet perovskite films led to a loss of uniformity. To address this, we used a controlled flow of nitrogen gas, “gas blowing”, across the surface to improve the uniformity of the film. The printed \( \text{PbI}_2 \) layer was converted by dipping it into a \( \text{CH}_3\text{NH}_3\text{I} \) solution in 2-propanol as described in the literature. The gas blowing process was also required following the dipping process to dry excess solvent quickly. Without gas blowing, the film turned to dark black, instead of reddish brown, and developed a rough surface which could be seen by eye. This can be due to large perovskite crystal growth. No working devices were obtained from such films. As a hole transporting layer (HTL), we initially used P3HT instead of high performing spiro-OMeTAD due to a lack of availability of the latter. The P3HT layer was spin coated on top of the perovskite layer and the device was completed by evaporating silver as an electrode. This device performed well with a PCE of over 11% as shown in Figure 5. This compares very favorably with reported PCEs of around 10% for devices using a P3HT HTL.\[30\] The result is very promising as it proves that the perovskite layer can also be fabricated by a roll-to-roll compatible process. Moreover, no high temperature sintering process was involved. We are currently further developing printed perovskite devices using the 3D printer to rapidly assay printing conditions and configurations. Details of the optimization process for fully printed perovskite solar cells will be published separately.

In conclusion, we have demonstrated how a 3D-printing platform can be used to fabricate solution-processed solar cells. 3D-printed parts were used to modify a 3D printer to be used for solution coating/printing. The printer was used to produce 1D continuous coatings, as well as 2D printing. PCEs of over 6% were obtained from a printed bulk heterojunction solar cell and the coating conditions were then transferred to large-sized modules. A 47.3 cm\(^2\) size module showed a power conversion efficiency of 4.57%, the highest value reported in the literature for a printed module. The first printed perovskite solar cell with a PCE of over 11% was also demonstrated. This communication demonstrates the versatility of the printer and the potential of fully automated production of solution-processed solar cells by this technology. With a full xyz control and a simple instruction set, the technology will be useful for the rapid realization of more innovative ideas in solution-processed solar cells as well as other electronic applications. The machine independent protocol, G code, suggests new paradigm of transferring process from machine to machine, lab to lab, and eventually lab to fab.

### Experimental Section

#### 3D Printer Setup

A 3D printer (Felix 2.0) was purchased and a stepper motor with a single shaft in the extruder was replaced by a generic NEMA 17 stepper motor with a dual shaft. A syringe pump was designed using open-source CAD software (FreeCAD). The design was exported to an STL file and the STL file was converted to G code by slicing software (Slic3r). The G code was printed using a 3D printer with a Repetier-Host interface. The printed part was assembled as shown in the Supporting Information. The printer was installed inside of a fume hood cabinet. Therefore, all coating experiments were carried out in air.

#### Device Fabrication

For small devices, ITO-coated glass (Shenzhen Display, 5 \( \Omega \text{sq}^{-1} \)) were successively sonicated for 5 min each in Deconex 12PA detergent solution, distilled water, acetone, and isopropanol. For 10 × 10 cm\(^2\) modules, ITO-glass (Lumtec, 5 \( \Omega \text{sq}^{-1} \)) were manually washed using Deconex 12PA detergent solution and rinsed by distilled water, acetone, and isopropanol. The substrates were then exposed to a UV-ozone (Novascan PDS-UVT) clean at room temperature for 10 min. For conventional configuration devices, PEDOT:PSS (HC Starck, Baytron P AI 4083) was deposited on the substrates through a syringe filter (0.2 \( \mu \text{m} \) RC filter) and spin coated at 5000 rpm for 20 s. The PEDOT/PSS layer was then annealed on a hotplate at 140 °C for 10 min in air. For inverted configuration devices, the ZnO precursor solution was prepared following a literature procedure.\[30\] The solution was spin coated on the cleaned ITO substrate at 5000 rpm for 40 s. The film was annealed at 140 °C for 10 min in air.

P3HT:PCBM solutions were prepared by dissolving P3HT (30 mg, Merck) and PCBM (24 mg, Nano-C) separately in chlorobenzene (1 mL) for each at 70 °C with stirring for more than 2 h. The solutions were cooled down to room temperature, mixed and filtered by a syringe filter (0.2 \( \mu \text{m} \) RC filter). Spin coated P3HT:PCBM layers were fabricated at 2000 rpm for 30 s onto 3D-printed layers were fabricated at 3 mm s\(^{-1}\) coating speed. Conventional devices were made by evaporating 100 nm of Al (KJ Lesker) at \( <1\times10^{-6}\) mBar (Angstrom evaporation system) followed by postannealing at 150 °C for 5 min under an inert atmosphere.

PCDTBT:PCBM solutions were prepared by dissolving PCDTBT (10 mg, St-Jean Photochimie Inc.) and PC71BM (35 mg, Nano-C) in DCB (3 mL) at 70 °C for more than 24 h with stirring. After cooling down to room temperature, the solution could not be filtered by syringe filters. Therefore, particles were removed by a coarse glass frit filter. The solution was coated on a ZnO layer on ITO-coated glass using the slot-die head with a 50 \( \mu \text{m} \) shim. A shim with a 13 mm channel was used with same width meniscus guide. The gap between the meniscus guide and substrate was always fixed as close to 100 \( \mu \text{m} \) as possible by checking the gap using feeler gauges of 80, 100, and 130 \( \mu \text{m} \). A small gap could be seen after putting the 80 \( \mu \text{m} \) gauge into the gap and the 130 \( \mu \text{m} \) gauge would not fit into the gap, thus confirming that the gap was kept within the 80–130 \( \mu \text{m} \) range. Wet films were made at various coating speeds and the films were dried on the printing bed without any thermal treatment. For evaporated electrodes, the samples were transferred to a vacuum evaporator. A 10 nm layer of MoO\(_3\) (Sigma-Aldrich) and 100 nm of Ag (KJ Lesker) were deposited through a shadow

![Figure 5. J–V curve of an organometal halide perovskite solar cell with a configuration of ITO/ZnO/Printed CH\(_3\)NH\(_3\)PbI\(_3\)/doped-P3HT/Ag fabricated by the 3D printer.](image-url)
mask to give an active area of 10 mm². For the printed electrodes, PEDOT:PSS (Ag6s EL-P 5010 + 50 wt% methanol) was coated using the 100 µm thick shim due to the high viscosity of the solution. A 4 mm width channel was used to produce 20 mm² devices. The active area was defined by an overlap area of a 5 mm ITO stripe and 4 mm PEDOT:PSS stripes. Silver (DuPont PV416) grids were made using a 21G blunt needle with 3 µL cm⁻² ink flow and 20 mm s⁻¹ coating speed.

Perovskite solar cells were fabricated on the same ITO substrates as for the BHJ solar cells. ZnO nanoparticle solutions were prepared by following literature procedures[9] and a 20 mg mL⁻¹ solution was spin-coated on UV/ozone treated ITO glass at 1000 rpm for 30 s. The ZnO layer was annealed at 120 °C for 10 min. A PbI₂ (99%, Sigma-Aldrich) solution (0.7 w, 322 mg mL⁻¹) in DMF was prepared by stirring at 70 °C for 1 h. The solution was cooled down to rt. and transferred to the slot-die head without filtration. In this case, a 200 µm gap between the nozzle and substrate was used to maximize the thickness of the wet film. Coating was carried out at 5 mm s⁻¹ with a 1 µL cm⁻² solution per slot-die head without filtration. In this case, a 200 µm gap between the nozzle and substrate was used to maximize the thickness of the wet film. Coating was carried out at 5 mm s⁻¹ with a 1 µL cm⁻² solution feed. The wet film was then dried by N₂ gas blowing (25 L min⁻¹ through 1 × 13 mm nozzle from ≈15mm distance) and kept in an enclosed sample carrier until the next step. CH₃NH₃I was synthesized following a literature procedure[32] and a 20 mg mL⁻¹ in ethanol solution was spin-coated on the perovskite film at 600 rpm for 12 s and then 3000 rpm for 40 s. The films were transferred to a glove box and 100 nm of Ag was deposited as described for BHJ solar cells.

**Measurement:** The thickness of films was measured by a Dektak 6 M surface profiler. The JV characteristics of the small devices were measured in an inert atmosphere with a computer-controlled Keithley 2400 Source Measure Unit. A 150 W Xenon lamp (XE lamp) (Newport) coupled with an AM 1.5G solar spectrum filter was used as the light source. Light was illuminated through a quartz window of the glove box and intensity was calibrated and monitored using a secondary reference cell (Hamamatsu S1133, with KG-5 filter, 2.8 × 2.4 mm of photosensitive area) which was calibrated by a certified reference cell (PVMeasurements, certified by NREL) under 1000 W/ m² AM 1.5G illumination from an Oriel AAA Research cell effciency records, http://www.nrel.gov/ncpv, accessed: September 2014.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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