A Fast Deposition-Crystallization Procedure for Highly Efficient Lead Iodide Perovskite Thin-Film Solar Cells**

Manda Xiao, Fuzhi Huang, Wenchao Huang, Yasmina Dkhissi, Ye Zhu, Joanne Etheridge, Angus Gray-Weale, Udo Bach, Yi-Bing Cheng,* and Leone Spiccia*

Abstract: Thin-film photovoltaics based on alkylammonium lead iodide perovskite light absorbers have recently emerged as a promising low-cost solar energy harvesting technology. To date, the perovskite layer in these efficient solar cells has generally been fabricated by either vapor deposition or a two-step sequential deposition process. We report that flat, uniform thin films of this material can be deposited by a one-step, solvent-induced, fast crystallization method involving spin-coating of a DMF solution of CH$_3$NH$_3$PbI$_3$ followed immediately by exposure to chlorobenzene to induce crystallization. Analysis of the devices and films revealed that the perovskite films consist of large crystalline grains with sizes up to microns. Planar heterojunction solar cells constructed with these solution-processed thin films yielded an average power conversion efficiency of 13.9 ± 0.7% and a steady state efficiency of 13% under standard AM 1.5 conditions.

Thin-film solar cells, such as dye-sensitized solar cells,[3] organic photovoltaics, [2] and colloidal nanocrystal solar cells,[3] can be assembled with low-cost materials and manufactured with cost-effective methods, and are considered very promising renewable energy technologies. Recently, alkylammonium lead(II) halides, such as CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbI$_2$Cl$_2$,[4] have been shown to be efficient photovoltaic materials with excellent light harvesting, high carrier mobility, and facile solution processability.[4-31] These organic-inorganic lead(II) complexes crystallize in the well-known perovskite structure with general formula AX$_3$. Perovskite solar cells utilizing a mesoporous scaffold, such as titania or alumina, the lead iodide light absorber, and an organic hole transport material (HTM), typically spiro-OMeTAD (2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-bifluorene) have achieved a power conversion efficiency (PCE) of >10%.[6,7] The PCEs were improved to 15% by using a two-step sequential deposition technique, involving spin-coating of a PbI$_2$ followed by exposure to a solution of CH$_3$NH$_3$I to form CH$_3$NH$_3$PbI$_3$, or a dual-source vapor-deposition technique to fabricate a planar heterojunction solar cell.[16-18]

Compared to the mesostructured perovskite solar cells, in which the light absorber is typically deposited on a 300 nm mesoporous scaffold, planar devices lacking this scaffold, have attracted interest because of their simpler structure.[17,18] To avoid the shunting in such planar devices, a nonporous homogenous perovskite film must be deposited. However, films produced by the conventional spin-coating methods were found to be composed of large CH$_3$NH$_3$PbI$_3$ grains and many uncovered pin-hole areas.[16] This structure arose from slow crystallization owing to the high boiling point of DMF (N,N-dimethylformamide, 153°C), and crystal growth arising from a slow nucleation rate during natural drying process in spin-coating. To date, the CH$_3$NH$_3$PbI$_3$ layer in the most efficient planar solar cells has been fabricated by either vapor deposition, a two-step sequential solution deposition, or a vapor-assisted two-step reaction process.[16,17,20] The vapor-deposition process is likely to increase the manufacturing cost whereas the sequential two-step deposition procedure will involve longer overall processing time.[16] Therefore, a faster, facile solution-processing technique that can regulate the perovskite crystallization process and produce high-quality films with controlled morphology is highly desirable for the construction of planar devices with superior performances.

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Attempts have been made to control the crystallization of CH$_3$NH$_3$PbI$_3$ during solution-processing by partially substituting I$^-$ with Cl$^-$ to create lattice distortions or introducing additives, such as 1,8-dio dooctane, to enhance the crystallization. Although good PCEs of approximately 12% were achieved, they were limited by quality of the perovskite films.

Herein, we report a one-step, solvent-induced, fast crystallization-deposition (FDC) method that results in flat, highly uniform CH$_3$NH$_3$PbI$_3$ thin films. This simple approach involves the spin-coating of a DMF solution of CH$_3$NH$_3$PbI$_3$ on a substrate, followed immediately by exposure of the wet film to a second solvent, such as chlorobenzene (CBZ), to induce crystallization. This FDC spin-coating method offers the advantage of single-step processing and short depositions time as the film formation is complete within 1 min. Perovskite films consisting of highly crystalline single grains are produced which when used to construct planar heterojunction solar cells yielded a maximum PCE of 16.2% under standard AM 1.5 conditions. Moreover, the process is highly reproducible with average efficiencies of 13.9 ± 0.7% for 10 devices prepared in one batch. We believe that this facile method can be applied for the fast production of highly efficient CH$_3$NH$_3$PbI$_3$ based solar cells.

The FDC method for preparing the CH$_3$NH$_3$PbI$_3$ films is shown in Figure 1. First, a dense TiO$_2$ layer (ca. 30 nm thick) was deposited on a fluorine-doped tin oxide (FTO) coated glass using spray pyrolysis. A DMF solution of CH$_3$NH$_3$PbI$_3$ (45 wt %) was then spin-coated on the TiO$_2$ layer at 5000 rpm. After a specific delay time (e.g., 6 s), a second solvent was quickly added to the substrate. The role of the second solvent is to rapidly reduce the solubility of CH$_3$NH$_3$PbI$_3$ in the mixed solvent and thereby promoting fast nucleation and growth of the crystals in the film. A series of 12 solvents was tested, including chlorobenzene, benzene, xylene, toluene, methanol, ethanol, ethylene glycol, 2-propanol, chloroform, THF, acetonitrile, and benzonitrile. An instant darkening of the film when the second solvent was added was taken as evidence of the formation of the desired material. In contrast, during a conventional spin-coating process where no second solvent was added, the wet film dried slowly and a shiny-gray film composed of non-uniform large crystals as a result of slow crystallization. In the FDC process (bottom), a second solvent (e.g. chlorobenzene) introduced on top of the wet film during the spin-coating process induces fast crystallization of uniformly sized perovskite grains.

Figure 2. Morphological and structural characterization of CH$_3$NH$_3$PbI$_3$ films prepared by FDC and a conventional spin-coating process. The concentration of the perovskite solution was 45 wt%. a) Low- and high-magnification SEM images of the surface of a CH$_3$NH$_3$PbI$_3$ film prepared by FDC with the addition of chlorobenzene. b) An atomic resolution TEM image of a CH$_3$NH$_3$PbI$_3$ grain from a film produced by FDC and a conventional spin-coating process. The central area in the films was non-uniform when 2-propanol or chloroform was introduced (images not shown) while the grain morphology in the films obtained with the addition of chlorobenzene, benzene, xylene and toluene are uniform over the entire substrate. We used chlorobenzene as a representative solvent in further studies. The transmission electron microscopy (TEM) image of the CH$_3$NH$_3$PbI$_3$ film prepared with chlorobenzene addition reveals clear lattice fringes (Figure 2c) indicating the formation of a crystalline structure with a lattice spacing of (0.31 ± 0.01) nm, which could be indexed as (004) or (220) of the tetragonal CH$_3$NH$_3$PbI$_3$ phase. This was further confirmed by the X-ray diffraction (XRD) patterns (Figure 2f). Intense diffraction peaks at 14.08°, 23.48°, 28.40°, and 31.86° can be respectively assigned to (110), (211), (220), and (310)

Information Figure S1a–e). The central area in the films was non-uniform when 2-propanol or chloroform was introduced (images not shown) while the grain morphology in the films obtained with the addition of chlorobenzene, benzene, xylene and toluene are uniform over the entire substrate. We used chlorobenzene as a representative solvent in further studies. The transmission electron microscopy (TEM) image of the CH$_3$NH$_3$PbI$_3$ film prepared with chlorobenzene addition reveals clear lattice fringes (Figure 2c) indicating the formation of a crystalline structure with a lattice spacing of (0.31 ± 0.01) nm, which could be indexed as (004) or (220) of the tetragonal CH$_3$NH$_3$PbI$_3$ phase. This was further confirmed by the X-ray diffraction (XRD) patterns (Figure 2f). Intense diffraction peaks at 14.08°, 23.48°, 28.40°, and 31.86° can be respectively assigned to (110), (211), (220), and (310)
with large PbI₂ crystals was obtained in ethanol, and ethylene glycol, a yellow film with high solubility, for example, methanol, acetone, and benzonitrile, in which CH₃NH₃PbI₃ is moderately soluble, produced an almost transparent film (Figure S1i). In contrast to the film obtained by FDC, the shiny-gray film obtained by conventional spin-coating contains larger rod-like grains with an incomplete coverage on the substrate (Figure 2d), which is in accordance with previous observations. A closer examination of these large rod grains reveals that the grain structure is similar to that of CH₃NH₃PbI₃ obtained by FDC (Figure 2e). This is further confirmed by the XRD patterns obtained for both films (Figure 2f). An advantage of the FDC method is that the thickness of the perovskite film can be easily controlled by changing the concentration of the perovskite solution, thus, films with a thickness of 150, 260, 350, and 550 nm were prepared from DMF solutions containing 25, 35, 45, and 55 wt % of CH₃NH₃PbI₃, respectively. Larger grain sizes were also found for the thicker films (Figure S2). The UV-Vis spectra indicate that, in the 350–700 nm region, 80–90% of the light passing through the FTO glass was absorbed by a 350 nm film and over 90% absorption for a 550 nm thick film (Figure S3). Most significantly, the morphology of the FDC processed CH₃NH₃PbI₃ thin films is remarkably different from the majority of film microstructures produced by solution-based approaches. Flat polygonal grains with triple junction grain boundaries are a predominant microstructural feature in our films, suggesting close packing of perovskite grains of a similar size along the film thickness direction. This characteristic may lead to improved charge transport properties for photovoltaic devices.

To further probe the film formation process using FDC, we investigated the addition of the chlorobenzene solution onto the spinning wet films to initiate nucleation and crystal growth after different delay times from the start of spinning, 2, 4, or 8 s. Figure S4 shows the morphologies of the obtained CH₃NH₃PbI₃ films. To understand these observations, we can divide the spin-coating process into three stages. In the first three seconds after spinning was commenced (stage 1), removal of excess precursor solution is a dominant process. Introduction of chlorobenzene at this stage did not lead to full surface coverage possibly because the perovskite solution was far from supersaturation (Figure S4a,d). In stage 2 (4–6 s), evaporation of the residue solvent occurs significantly concentrating the perovskite solution from which a dense and uniform film was formed when the second solvent was introduced (Figure S4b,e). In stage 3 (after 7 s), the liquid film started to dry and heterogeneous crystallization occurs. Addition of chlorobenzene at this stage did not help to achieve a homogeneous perovskite film (Figure S4c,f).

Solar cells were constructed with the perovskite films produced by the optimized FDC method. Figure 3a,b illustrate the planar device structure and a cross-sectional SEM image, fabricated by focused ion beam (FIB) milling. Although gallium ion beam etching induced slight shrinkage of the spiro-OMeTAD layer at the cross-section, which is responsible for electron charging and a bright contrast at the edge of the CH₃NH₃PbI₃ layer, the optimized device can be seen to be clearly composed of a 30 nm thick dense TiO₂ layer on FTO, a 350 nm perovskite layer, a 180 nm spiro-OMeTAD layer, and a 70 nm thermally evaporated Ag layer as the back contact. Solar cells were also fabricated using FDC prepared CH₃NH₃PbI₃ films of different thickness and the films prepared by the conventional spin-coating techniques. The average photovoltaic parameters (Table 1) of these cells were measured under simulated AM 1.5G illumination at an intensity of 100 mW cm⁻².

Solar cells utilizing the films prepared by conventional spin-coating exhibited a poor PCE of only 1.5%, mainly because of cell shunting and poor light absorption arising from incomplete surface coverage. In contrast, solar cells utilizing a 150 nm perovskite layer, produced by FDC, yielded a higher Jₑₒ of 17 mA cm⁻² and a much better PCE of 8%, revealing the importance of full coverage of the perovskite film on the substrate. Increasing the film thickness from 150 nm to 350 nm led to higher Jₑₒ and PCEs, which is mainly
attributed to the enhanced light absorption (Figure S2). A further increase in film thickness to 550 nm resulted in lower \(J_{oc}\) and \(V_{oc}\), possibly a result of increased charge recombination. The reproducibility of the results was tested by fabricating a batch of 10 devices with an optimized film thickness of 350 nm (Table S1). The average PCE of 13.9 \(\pm\) 0.7\% is higher than that achieved in previous studies using the two-step sequential deposition and vacuum-based vapor deposition methods\[^{16,17}\]. The high reproducibility is attributed to the high homogeneity of the CH\(_3\)NH\(_3\)PbI\(_3\) film achieved by the FDC technique. Recently an anomalous hysteresis in the \(J-V\) curves of perovskite solar cells has been observed\[^{37,38}\]. We therefore recorded the \(J-V\) curves of a typical solar cell prepared by the FDC method with different scanning directions (Figure 3c). A PCE of 13.8\% was recorded when using the conventional scan direction from forward bias (FB) to short circuit (SC) with a scan rate of 0.1 \(\text{Vs}^{-1}\) while the opposite scan direction yielded an efficiency of 11.6\%. We also recorded the photocurrent of this cell held at a forward bias of 0.77 \(\text{V}\) as a function of time to gain some understanding of the stabilized power output under working conditions (Figure 3d). The photocurrent stabilizes within seconds to approximately 17 \(\text{mAcm}^{-2}\), yielding a stabilized power conversion efficiency of 13.0\%, measured after 600 s. This indicates that FB to SC scans provide a more accurate representation of the cell’s photovoltaic performance while still resulting in a relative overestimation of the steady state power output by about 5.8\%.

The \(J-V\) curves were also recorded with scan rates ranging from 0.1 \(\text{Vs}^{-1}\) to 0.01 \(\text{Vs}^{-1}\) (Figure S5), revealing a weak scan-rate dependence of the hysteresis effect. In addition, for one cell measured under a light intensity of 100 \(\text{mWcm}^{-2}\) with a scanning direction from FB to SC and a scan rate of 0.1 \(\text{Vs}^{-1}\), the \(J_{sc}\), \(V_{oc}\), and fill factor are 21.1 \(\text{mAcm}^{-2}\), 1.04 \(\text{V}\), and 0.74, respectively, yielding a PCE of 16.2\% (Figure S6a). The incident photon-to-electron conversion efficiency (IPCE) of the device, shown in Figure S6b, exhibits a photocurrent onset at 800 nm and rises steeply to 76\% at 760 nm, in agreement with the band gap of CH\(_3\)NH\(_3\)PbI\(_3\) and previous studies\[^{15-19}\]. IPCEs above 80\% can be observed across a broad spectral region from 400–700 nm, and especially in the 400–600 nm range. Integration of the IPCE spectrum with the AM1.5G photon flux yields a current density of 21.5 \(\text{mAcm}^{-2}\), which is in excellent agreement with the measured photocurrent density of 21.1 \(\text{mAcm}^{-2}\). Further improvements in \(J_{sc}\) would be anticipated if the light absorption in the NIR region could be enhanced by utilizing, for example, plasmonic technologies\[^{39}\].

To investigate in detail the microstructure of the CH\(_3\)NH\(_3\)PbI\(_3\) film produced by FDC, the cross-section of the grain structures was further characterized by TEM. Special care was taken to minimize the sample damage during cross-section fabrication by FIB milling. However, as shown in the bright-field TEM image (Figure S7), some milling damage is evident in the perovskite layer. Nevertheless, the macroscopic geometry of the film is retained and reveals, as expected, a 350 nm-thick CH\(_3\)NH\(_3\)PbI\(_3\) layer on a dense TiO\(_2\) layer, which shows a granular structure with grain sizes comparable to the layer thickness. No horizontal grain boundary is observed, suggesting that most perovskite grains span the thickness of the film. Grains without obvious FIB damage were selected and examined in more detail using selected-area-diffraction (SAD) and high resolution TEM. The perovskite was sensitive to electron beam irradiation unless care was taken to minimize the dose. Figure 4 shows the atomic resolution images from the top and bottom region of an individual perovskite grain, along with a SAD pattern from a much larger region in the center of the same grain. The lattice fringes in the two images have the same orientation (Figure 4b,d). In addition, the Fourier transform of these images and the SAD pattern all show the same strong perovskite diffraction spots aligned with the same orientation (Figure 4c,e), consistent with the whole perovskite grain

![Figure 4](https://www.angewandte.org)

**Figure 4.** Characterization of the CH\(_3\)NH\(_3\)PbI\(_3\) perovskite grain structures. a) TEM cross-sectional image of the FTO/TiO\(_2\)/CH\(_3\)NH\(_3\)PbI\(_3\)/Spiro-OMeTAD/Ag solar cell. Inset: SAD pattern taken from the region indicated by the circle. The boundaries of the selected grain are highlighted with dotted lines. b,d) Atomic resolution TEM images of the top and bottom region of an individual perovskite grain. c,e) Fourier transforms of (b) and (d), respectively. The major perovskite diffraction spots are indexed in white with a subscript T (tetragonal). The weaker diffraction spots indicated by arrows can be indexed as 130 from the tetragonal perovskite phase, but may also originate from a second phase.

**Table 1:** Device parameters for solar cells using perovskite films with different thicknesses prepared by conventional spin-coating and FDC.\[^{34}\]

<table>
<thead>
<tr>
<th>Cell</th>
<th>(V_{oc}) [V]</th>
<th>(J_{sc}) [mAcm(^{-2})]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>0.52 (\pm) 0.05</td>
<td>5.6 (\pm) 0.9</td>
<td>0.61 (\pm) 0.01</td>
<td>8.0 (\pm) 0.1</td>
</tr>
<tr>
<td>FDC, 150 nm</td>
<td>0.77 (\pm) 0.08</td>
<td>17.0 (\pm) 0.2</td>
<td>0.63 (\pm) 0.01</td>
<td>11.7 (\pm) 0.3</td>
</tr>
<tr>
<td>FDC, 260 nm</td>
<td>0.96 (\pm) 0.13</td>
<td>19.3 (\pm) 0.3</td>
<td>0.68 (\pm) 0.03</td>
<td>13.9 (\pm) 0.7</td>
</tr>
<tr>
<td>FDC, 350 nm</td>
<td>0.98 (\pm) 0.01</td>
<td>21.0 (\pm) 0.9</td>
<td>0.60 (\pm) 0.02</td>
<td>11.7 (\pm) 0.2</td>
</tr>
<tr>
<td>FDC, 550 nm</td>
<td>0.97 (\pm) 0.22</td>
<td>20.3 (\pm) 0.2</td>
<td>0.60 (\pm) 0.02</td>
<td>11.7 (\pm) 0.2</td>
</tr>
</tbody>
</table>

[a] data for “FDC, 350 nm” is averaged from 10 devices and 4 devices for others.
being a single crystal. However, other weak reflections are also evident in these diffraction patterns. This may be due to localized loss of CH$_3$NH$_3$I under ion (and possibly electron) beam irradiation, leaving small regions of PbI$_2$, possibly on the surface. Because the (220) and (004) lattice spacings in the tetragonal perovskite phase are very similar to each other (both ca. 0.31 nm) and cannot be distinguished by our SAD or TEM study. Therefore, all the diffraction spots that are indexed as 220T could also be indexed as 004T. The single perovskite grains are believed to facilitate charge transport between electrodes because of the reduced number of defect and trap states at grain boundaries.[40] In addition, almost all the grains examined had no grain boundaries parallel to the plane of the two electrodes, which can lead to reduced electron scattering during charge transport. Both effects can contribute to efficient charge extraction. SAD patterns were also taken from 16 individual perovskite grains along the length of the perovskite layer (Figure S7). The specimen area illuminated by the electron beam in each case is a circle with a diameter of approximately 200 nm. As with the grain in Figure 4, most grains show strong primary diffraction spots associated with a single crystal of the tetragonal perovskite phase together with a number of weak diffraction spots, the majority of which are consistent with the FIB-induced PbI$_2$ phase. It is also evident that adjacent perovskite grains do not appear to share a common crystallographic axis.

In conclusion, a fast, single-step, solution-based deposition-crystallization method has been developed, which allows control over the dynamics of nucleation and grain growth of CH$_3$NH$_3$PbI$_3$, and achieves the rapid and reproducible fabrication of high-quality perovskite thin films. SEM analysis indicated that the perovskite thin films of controllable thickness can be prepared with large grain structures that fully cover the substrate. The application of these films in photovoltaic technologies, such as silicon-based solar cells electrodes. The simplicity and the low-temperature solution process characteristic of the FDC protocol is fully compatible with the construction of tandem devices using existing photovoltaic technologies, such as silicon-based solar cells and polymer solar cells.[11] We believe that this thin-film processing technology will not only benefit the perovskite-based photovoltaic devices but also bring new possibilities to perovskite-based hybrid optoelectronic devices, such as field effect transistors and light emitting diodes.

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Supplementary Information

METHODS

Materials. Unless specified otherwise, all materials were purchased from either Alfa Aesar or Sigma-Aldrich and used as received. Spiro-MeOTAD was purchased from Merck KGaA and Luminescence Technology Corp. CH$_3$NH$_3$I was synthesized according to a previous study. (Im, J.-H., Lee, C.-R., Lee, J.-W., Park, S.-W. & Park, N.-G. Nanoscale 2011, 3, 4088–4093)

Device fabrication. Firstly, FTO-coated glass substrates (TEC8, Dyesol) were patterned by laser cutting and washed by ultrasonication with soap (5% Hellmanex in water), deionized water, and ethanol. A 30-nm-thick dense layer of TiO$_2$ was then coated on the substrates by spray pyrolytic deposition of a bis(isopropoxide)bis(acetylacetonato)titanium(IV) solution (75% in 2-propanol, Sigma-Aldrich) diluted in 2-propanol (1:9, volume ration) at 450 °C. FTO glasses with dense TiO$_2$ layers were used within 2 weeks of their preparation.

The synthesized CH$_3$NH$_3$I (0.200 g) was mixed with PbI$_2$ (0.578 g) in anhydrous N,N-dimethylformamide (1 mL) by shaking at room temperature for 20 min to produce a clear CH$_3$NH$_3$PbI$_3$ solution with concentration of 45 wt%. CH$_3$NH$_3$PbI$_3$ solutions with concentrations of 25, 35 and 55 wt% were prepared in a similar manner. To deposit perovskite films, the CH$_3$NH$_3$PbI$_3$ solution (50 µL) was first dropped onto a TiO$_2$ coated FTO substrate (substrate area ~1 cm x 1 cm). The substrate was then spun at 5000 rpm and after six seconds anhydrous chlorobenzene (150 µL) was quickly dropped onto the center of the substrate. This instantly changed the color of the substrate from transparent to light brown. For comparison, the effect of adding chlorobenzene after 2, 4 and 8 seconds after starting of spinning on film crystallization was also tested. For the conventional spin-coating method, the perovskite solution was spun at 5000 rpm for 30 s. The obtained films were then dried at 100°C for 10 min.

The hole-transporting material was deposited by spin coating at 2200 rpm for 30 s. The spin coating solution was prepared by dissolving 52.8 mg spiro-MeOTAD, 10 µL of a stock solution of 500 mg mL$^{-1}$ lithium bis(trifluoromethylsulphonyl)imide in acetonitrile and 14.4 µL 4-tert-butylpyridine in 640 µL chlorobenzene. Device fabrication was finally completed by thermal evaporation of a 70-nm-thick film of silver as the cathode. Devices were left in a desiccator overnight and tested next day. Note that the best performing cell was made using spiro-MeOTAD from Luminescence Technology Corp., while other cells were made using spiro-MeOTAD from Merck KGaA. Device fabrication was carried out in a N$_2$-filled glove box.

Characterization. A sun simulator (Oriel) fitted with a filtered 1,000W xenon lamp was used to provide simulated solar irradiation (AM1.5, 100mW cm$^{-2}$). Current-voltage characteristics were measured using a Keithley 2400 source meter. The output of the light source was adjusted using a calibrated silicon photodiode (Peccell Technologies). The
photodiode was fitted with a color filter provided by the supplier to minimize the optical mismatch between the calibration diode and the solar cells. The solar cells were masked with a non-reflective metal aperture of 0.16 cm$^2$ to define the active area of the device and avoid light scattering through the edges. IPCE spectra were recorded using a 150W xenon lamp (Oriel) fitted with a monochromator (Cornerstone 260) as a monochromatic light source. The illumination spot size was slightly smaller than the active area of the test cells. IPCE photocurrents were recorded under short-circuit conditions using a Keithley 2400 source meter. The monochromatic photon flux was quantified by means of a calibrated silicon photodiode (Peccell Technologies). The surface morphology of perovskite films was investigated using an FEI Nova NanoSEM 450 microscope operating at 5 kV. The cross section images were performed with a FEI Nova dual beam, focused ion beam system, combined SEM and gallium ion beam instrument. Prior to performing the cross section, two Pt protecting layers were deposited in situ with an electron beam source at 6.3 nA and ion beam source at 0.30 nA. Milling of the cross sections was achieved with a gallium ion source at a 52° tilting angle. The TEM images were taken using a FEI Tecnai G2 F20 microscope. The absorption spectra of the perovskite films were measured on a PerkinElmer Lambda 950 UV/VIS/NIR spectrometer. X-ray diffraction (XRD) experiments were conducted by a Philips X-ray diffractometer with Cu K$\alpha$ radiation. The samples were scanned from 10° to 60° with a step-size of 0.02°.
Figure S1. SEM images of CH$_3$NH$_3$PbI$_3$ perovskite films prepared by FDC using different second solvents. a) toluene, b) benzene, c) xylene, d) chloroform, e) 2-propanol, f) ethanol, g) methanol, h) ethylene glycol, i) THF. Inset in each picture is a higher magnification image of the same film.
**Figure S2.** SEM images of CH$_3$NH$_3$PbI$_3$ perovskite films prepared by FDC using different concentrations of perovskite solutions. a,d) 25 wt%, b,e) 35 wt%, c,f) 55 wt%.

**Figure S3.** UV-Visible spectra of CH$_3$NH$_3$PbI$_3$ perovskite films prepared by FDC using different concentrations of perovskite solutions in DMF.
**Figure S4.** SEM images of the surface morphology of the CH$_3$NH$_3$PbI$_3$ films prepared by adding a CBZ solution at different delay times from the start of the spin-coating process. a,d) after two seconds; b,e) after four seconds; c,f) after eight seconds.

**Table S1:** Photovoltaic parameters of a batch of ten devices measured under 100 mW cm$^{-2}$ simulated AM1.5G illumination.

<table>
<thead>
<tr>
<th>Cell</th>
<th>$V_{oc}$</th>
<th>$J_{sc}$</th>
<th>FF</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>V</td>
<td>mA cm$^{-2}$</td>
<td></td>
<td>%</td>
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<tr>
<td>1</td>
<td>0.98</td>
<td>21.5</td>
<td>0.69</td>
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<tr>
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<tr>
<td>Average</td>
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<td>21.0 ± 0.9</td>
<td>0.68 ± 0.03</td>
<td>13.9 ± 0.7</td>
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**Figure S5.** Influence of scan rates on the $J$–$V$ characteristics for a device prepared by FDC protocol. The device was scanned from forward bias to short circuit (FB-SC, red) and from short circuit to forward (SC-FB, blue) under simulated AM1.5G solar irradiation of 100 mW cm$^{-2}$ at a range of scan rates from 0.01 V/s to 0.1 V/s. The scans start and finish under forward bias and have 1 min. of stabilization time under illumination prior to scanning.

**Figure S6.** a) $J$–$V$ curve of the best-performing solar cell measured at a simulated AM1.5G solar irradiation of 100 mW cm$^{-2}$ (solid line) and in the dark (dashed line). The $J$–$V$ curve was obtained by scanning from FB to SC with a scan rate of 0.1 V/s. b) IPCE spectrum of the solar cell corresponding to a).
Figure S7. TEM image of a device cross-section and SAD patterns taken from individual grains within the CH$_3$NH$_3$PbI$_3$ perovskite layer. In the SAD patterns, the CH$_3$NH$_3$PbI$_3$ diffraction spots are indexed in white with a subscript T (tetragonal), and the PbI$_2$ diffraction spots are indexed in blue. Damage due to FIB milling is indicated by red arrows. A number of weaker diffraction spots are evident, the majority of which are consistent with the PbI$_2$ phase. This is mainly due to FIB damage during sample preparation as well as some subsequent electron beam damage, as PbI$_2$ diffraction peaks, although present, are extremely weak in the XRD.