

Flexible high efficiency perovskite solar cells

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Flexible perovskite based solar cells with power conversion efficiencies of 7% have been prepared on PET based conductive substrates. Extended bending of the devices does not deteriorate their performance demonstrating their suitability for roll to roll processing

Broader context

Thin film photovoltaics represent the ultimate goal in the quest for clean renewable energy. Recently, methylammonium lead halide perovskites have been identified as promising absorbers for solar cells. Over the past three years, the performance of perovskite-based solar cells has rapidly improved reaching efficiencies as high as 15%. The perovskite absorbers are prepared from low-cost and abundantly available components allowing for the preparation of low cost photovoltaic devices and modules. However, to achieve very low cost devices they should be prepared using roll to roll (R2R) processes on large area flexible substrates. This requires a device architecture that does not need high temperature steps and that can be prepared using large area coating or printing methods. Here we show that methylammonium lead iodide perovskite layers when sandwiched in between two thin organic charge transporting layers and processed on a polymer based conductive substrate using large area compatible coating techniques lead to flexible solar cells with high power conversion efficiencies. Moreover, extended bending of these devices does not deteriorate their performance demonstrating the suitability of perovskite based solar cells for roll to roll processing.

Thin film photovoltaic devices hold great promise to reduce the dependencies on fossil energy.¹ After the seminal work of Miyasaka et al.,² tremendous progress in the performance of methylammonium lead iodide perovskite based solar cells has been made.^{3–12} The hybrid organic–inorganic methylammonium lead iodide perovskites, pioneered by Mitzi, have been recognized for their excellent semiconducting properties.^{13,14} The ease with which these organic–inorganic hybrid perovskite materials can be prepared and processed from solution has made them attractive for photovoltaic applications.¹⁵ All high efficiency perovskite solar cells reported until now use (mesoscopic) metal oxides such as Al₂O₃, TiO₂ or ZrO₂ requiring a high temperature sintering process. Ball et al. showed that a thick layer (350 nm) of the mixed halide methylammonium lead perovskite (CH₃NH₃PbI_{3-x}Cl_x) leads to efficient solar cells (12%).⁹ They argued that the perovskite functions as the absorber and as the electron and hole transporter. Additionally, it was suggested that the excitons predominantly dissociate in the bulk and not at a donor–acceptor interface. Hence, no bulk heterojunction between donor and acceptor is required to achieve efficient cells. This was confirmed by Liu et al., who showed that the mesostructured of the metal oxide is not required to prepare efficient (15.4%) perovskite based solar cells.¹² Recent results indicate that at least part of the excitons dissociate at the interface of the perovskite layer and the hole and electron transporting layer.^{16,17} An inverted layout, similar to that employed in small molecular weight and polymeric solar cells, has also been described.^{18,19} In these devices, the holes are extracted via the transparent conductor poly(3,4-ethylenedioxythiophene): poly(styrenesulfonic acid) (PEDOT:PSS). Recently, we have improved the performance of such inverted devices by sandwiching an evaporated CH₃NH₃PbI₃ perovskite in between organic electron and hole blocking layers, reaching a PCE of 12%.²⁰ In view of the above mentioned results the perovskite based solar cells are very well suited for roll to roll (R2R) processing on flexible substrates. It is not clear, however, how the perovskite

active layer will behave on a flexible substrate especially when it is bent. The perovskite is a crystalline material; hence, cracks or other imperfection may occur upon bending it

Here, we present a flexible thin \square lm solar cell based on a sublimated methylammonium lead iodide perovskite layer that is sandwiched in between two very thin electron and hole blocking layers consisting of organic molecules. A flexible transparent conductor based on a stack of thin layers of aluminium doped ZnO (AZO), silver and AZO was used (Fig. 1). Power conversion efficiencies (PCEs) as high as 7% were obtained and maintained when the solar cell was bent over a roll with a diameter of 5.5 cm for 50 times. No significant deterioration of the key performance parameters of the solar cell was observed indicating that the perovskite is compatible with roll to roll processing.

The flexible solar cell was prepared on 50 micron thick PET foil coated with a transparent silver electrode. The electrodes were produced by depositing a multilayer stack composed of AZO 30 nm/Ag 9 nm/AZO 30 nm, where AZO designates Al doped ZnO with 2 wt% Al. The coating was applied by DC magnetron sputtering in a batch coater. For the AZO planar ceramic targets were used. The process pressure was about 5×10^{-3} mbar. In the visual range, the electrode transparency was 81%, with a sheet resistance of 7.5 Ohm. The coating process can be easily transferred to large scale roll to roll coating.^{21,22} After cleaning the foils by rinsing them with ultrapure water and isopropanol a 70 nm poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) layer was deposited using spin coating and it was annealed for 15 minutes at 90° C. Following the PEDOT:PSS layer a thin layer (20 nm) of poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine] (polyTPD) was deposited by spin coating (Fig. 1), as the electron blocking layer. On top of this the CH₃NH₃PbI₃ was thermally evaporated to a thickness of 260 nm followed by a thin layer (30 nm) of [6,6]-phenyl C₆₁-butyric acid methylester (PCBM) as the hole blocking layer.²³ The device was completed by

the evaporation of an Au top electrode (70 nm). The PCBM layer was deposited using a meniscus coating process to ensure a high quality \square lm.²⁴ The thickness of the layers was established using absorbance measurements. Full details of the device fabrication and characterization are provided in the ESI.[†]

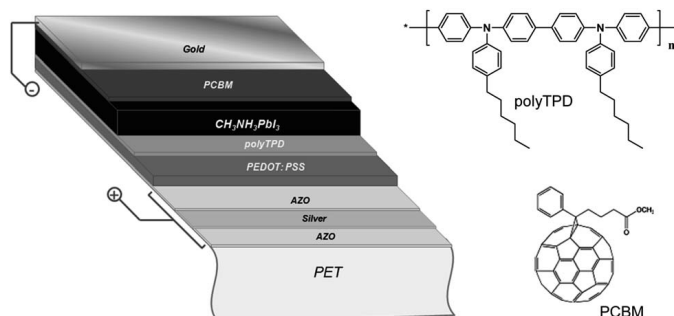


Fig. 1 Schematic layout of the flexible perovskite solar cell and chemical structure of the materials used as the electron and hole blocking layer.

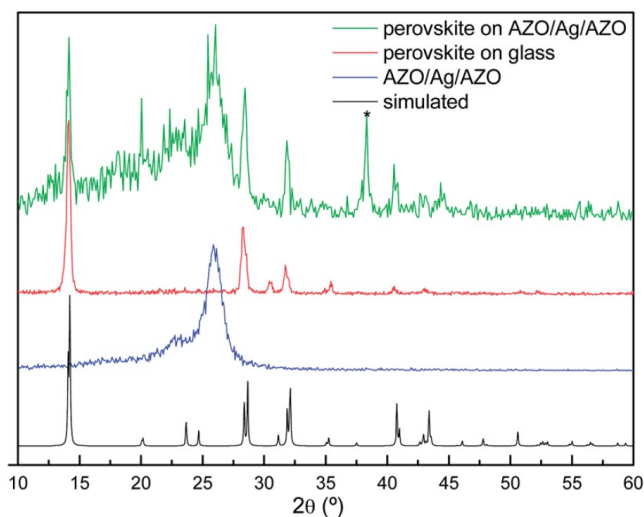


Fig. 2 Grazing incidence X-ray diffraction (GIXRD) pattern with $K\alpha_1$ radiation ($1 \frac{1}{4}$ 1.54056 \AA) of the sublimed thin film on AZO/Ag/AZO (green) compared with a film sublimed on glass (red),²⁰ the AZO/Ag/AZO substrate (blue) and the calculated one for CH₃NH₃PbI₃ (black). The star on the green diffractogram indicates a reflection of the gold used in the device.

The $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin films grown on the AZO/Ag/AZO substrates were characterized using grazing incidence X-ray diffraction (GIXRD). Fig. 2 shows the X-ray powder pattern of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film evaporated on an AZO/Ag/AZO substrate, revealing the formation of a crystalline layer. The sharp diffraction peaks of the perovskite can readily be identified. Interestingly, upon comparison with a perovskite thin film evaporated on glass it can be noted that no preferential orientation is observed on the flexible AZO/Ag/AZO substrates, in contrast to what happens in the case of glass.

Due to the small sample size the application of the hole blocking layer using meniscus coating is difficult. In particular, the thickness of this layer was not easy to control. Due to this we used a PCBM layer of approximately 30 nm which is thicker than needed. A scanning electron microscope (SEM) cross-section of the thin film device is shown in Fig. 3. The resolution of the image is limited by the charging of the sample at higher magnification.

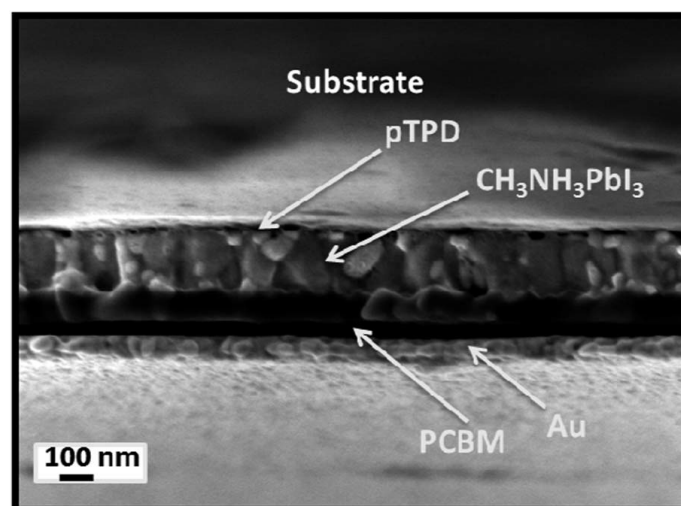


Fig. 3 SEM cross-section of the perovskite device on the PET foil. A thin graphite layer was deposited on top to prevent excessive charging during measurement.

Fig. 4a shows the current–voltage (J – V) characteristics of a typical small area (0.12 cm^2) flexible perovskite solar cell measured under light intensities of 100 mW cm^2 . The reproducibility from device to device was within 10%. The shortcircuit current density (J_{SC}), open-circuit

voltage (VOC) and \square ll factor (FF) for a typical device, respectively, are 14.3 mA cm², 1.04 V and 0.47, leading to a power conversion efficiency of 7%. Previously, on glass substrates JSC, VOC and FF of 16.1 mA cm², 1.05 V and 0.67, respectively, have been obtained leading to a PCE of 12%.²⁰

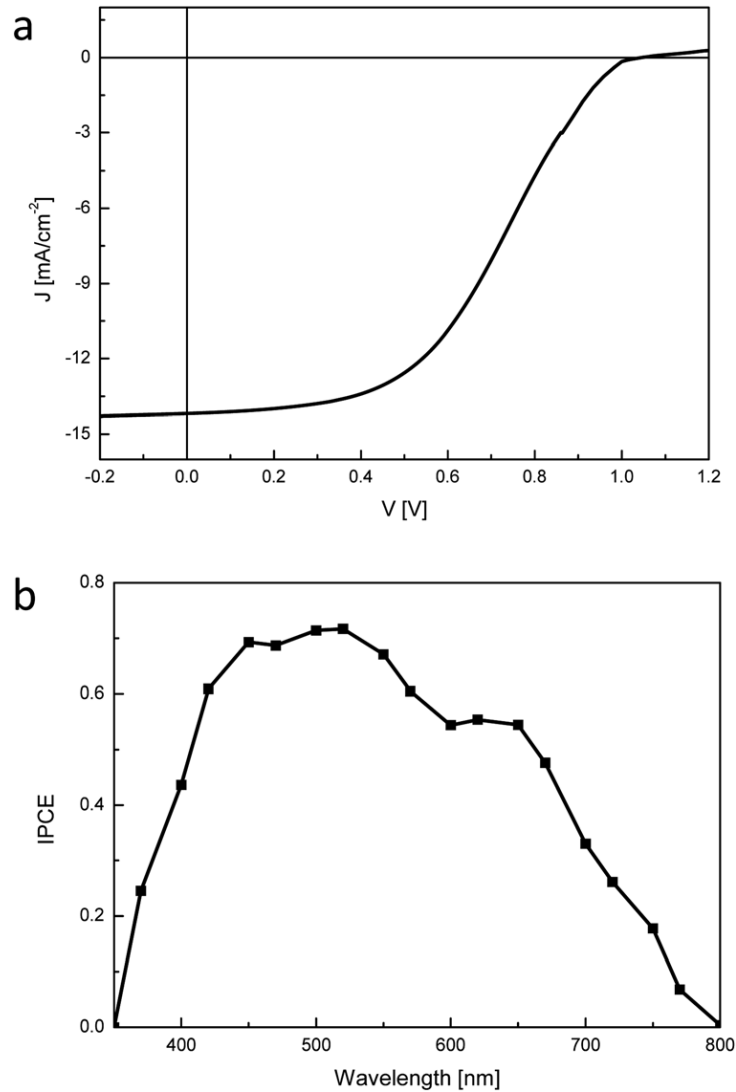


Fig. 4 Characterization of a typical solar cell. (a) Photocurrent density versus voltage at 100 mW cm². (b) IPCE spectrum.

Hence, the main difference between the devices on the glass substrates and on the foils is the lower FF which causes the strong reduction in the PCE. The main reason for this decrease in FF and PCE is due to the thicker hole and electron blocking layers in the \square exible cells. The increased thickness of these layers is caused by more difficult handling of the small area

flexible substrates. This can be solved when a larger substrate is used in either a batch or roll-to-roll (R2R) process employing slot-die coaters. The incident photon-to-current conversion efficiency (IPCE) spectra exhibit 74% (Fig. 4b) where the generation of photocurrent started at 790 nm in agreement with the band gap of the CH₃NH₃PbI₃.

In spite of the before mentioned shortcomings the PCE obtained is among the highest reported for flexible solar cells using organic molecules.^{25–27} Yet, more important than the actual value of the PCE is the effect that repeated bending of the substrate has on it. To investigate this, the flexible solar cells were bent over a roll with a diameter of 5.5 cm. The performance was evaluated up to 50 bending cycles and no reduction of the key performance indicators was observed. JSC and VOC remained identical throughout the test and the fill factor decreased slightly from 0.474 to 0.464 after 50 bending cycles, which lead to a decrease in the PCE of 0.1% (Fig. 5b).

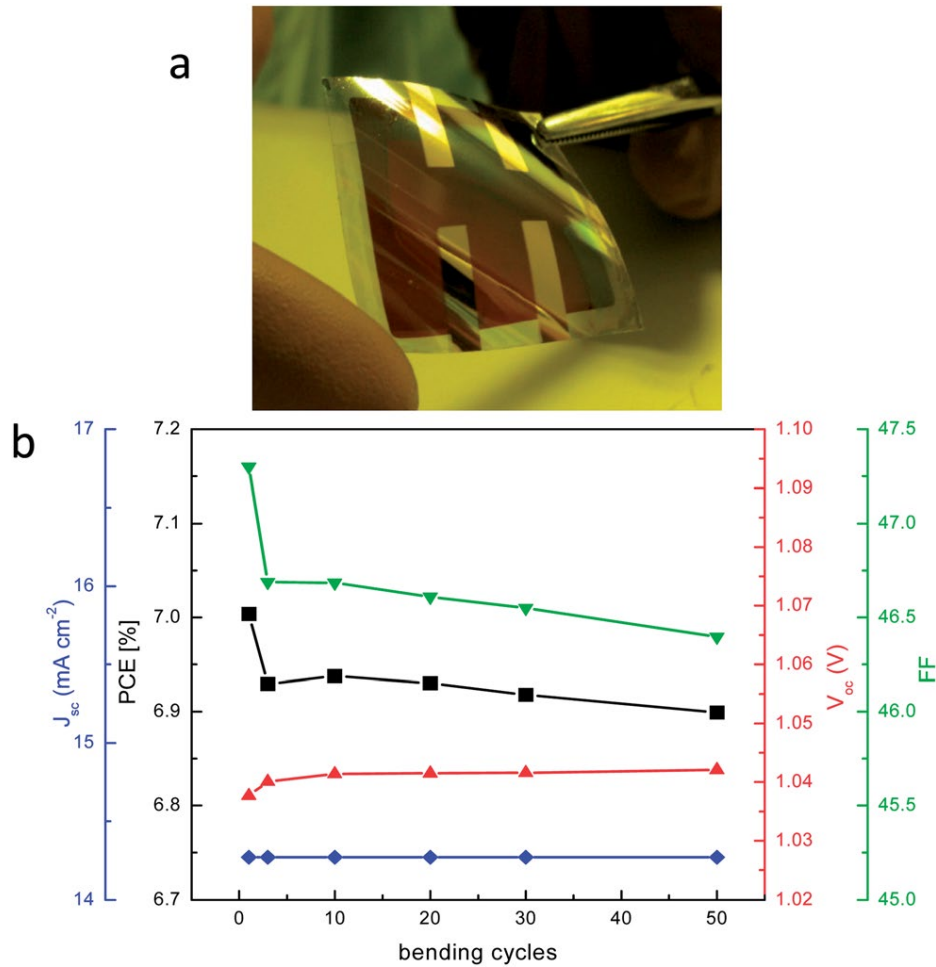


Fig. 5 Bending test of the flexible solar cells. (a) Photograph of the flexible solar cell. (b) PCE, FF, JSC and VOC as a function of bending cycles.

Conclusions

In summary, flexible solar cells based on the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite absorber have been prepared. The device layout is very compatible with flexible substrates because all the processes are performed at room temperature. The exception is the annealing at 90°C of the polymeric conductor (PEDOT:PSS) which is well below the critical temperature of most polymers. An AZO/Ag/AZO coated PET foil was used as the flexible substrate. In spite of some difficulties in controlling the thickness of the essential electron and hole blocking layers power conversion

efficiencies as high as 7% were obtained. More importantly, this solar cell layout is very robust leading to a decline of the power conversion efficiency of only 0.1% after 50 bending cycles. This demonstrates that the perovskite solar cells are very suitable for roll to roll production.

Acknowledgements

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Notes and references

- 1 S. B. Darling and F. You, *RSC Adv.*, 2013, 3, 17633–17648.
- 2 A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, *JACS*, 2009, 131, 6050–6051.
- 3 J.-H. Im, C.-R. Lee, J.-W. Lee, S.-W. Park and N.-G. Park, *Nanoscale*, 2011, 3, 4088–4093.
- 4 I. Chung, B. Lee, J. He, R. P. H. Chang and M. G. Kanatzidis, *Nature*, 2012, 485, 486–489.
- 5 L. Etgar, P. Gao, Z. Xue, Q. Peng, A. K. Chandiran, B. Liu, M. K. Nazeeruddin and M. Grätzel, *JACS*, 2012, 134, 17396–17399.

- 6 H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, S.-J. Moon, R. Humphry-Baker, J.-H. Yum, J. E. Moser, M. Gratzel and N.-G. Park, *Sci. Rep.*, 2012, 2, 591.
- 7 M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, 338, 643–647.
- 8 A. Abrusci, S. D. Stranks, P. Docampo, H.-L. Yip, A. K. Y. Jen and H. J. Snaith, *Nano Lett.*, 2013, 13, 3124–3128.
- 9 J. M. Ball, M. M. Lee, A. Hey and H. J. Snaith, *Energy Environ. Sci.*, 2013, 6, 1739–1743.
- 10 J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Gratzel, *Nature*, 2013, 499, 316–319.
- 11 J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C.-S. Lim, J. A. Chang, Y. H. Lee, H.-j. Kim, A. Sarkar, K. Nazeeruddin, M. Gratzel and S. I. Seok, *Nat. Photonics*, 2013, 7, 486–491.
- 12 M. Liu, M. B. Johnston and H. J. Snaith, *Nature*, 2013, 501, 395–398.
- 13 C. R. Kagan, D. B. Mitzi and C. D. Dimitrakopoulos, *Science*, 1999, 286, 945–947.
- 14 D. B. Mitzi, *J. Mater. Chem.*, 2004, 14, 2355–2365.
- 15 H. J. Snaith, *J. Phys. Chem. Lett.*, 2013, 3623–3630.
- 16 S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza and H. J. Snaith, *Science*, 2013, 342, 341–344.
- 17 G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Gratzel, S. Mhaisalkar and T. C. Sum, *Science*, 2013, 342, 344–347.
- 18 J.-Y. Jeng, Y.-F. Chiang, M.-H. Lee, S.-R. Peng, T.-F. Guo, P. Chen and T.-C. Wen, *Adv. Mater.*, 2013, 25, 3727–3732.

19 S. Sun, T. Salim, N. Mathews, M. Duchamp, C. Boothroyd, G. Xing, T. C. Sum and Y.-M. Lam, *Energy Environ. Sci.*, 2014, 7, 399–407.

20 O. Malinkiewicz, Y. Aswani, Y. H. Lee, M. Minguéz Espallargas, M. Graetzel, M. K. Nazee-ruddin and H. J. Bolink, *Nat. Photonics*, 2013, DOI: 10.1038/nphoton.2013.341.

21 T. Kroyer, A. Georg, M. Regnat, B. Zimmermann, U. Wuerfel and W. Graf, *Proceedings of the Large-area, Organic and Printed electronics Convention*, 2010.

22 M. Kohlstädt, M. Grein, P. Reinecke, T. Kroyer, B. Zimmermann and U. Würfel, *Sol. Energy Mater. Sol. Cells*, 2013, 117, 98–102.

23 G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, 270, 1789–1791.

24 O. Malinkiewicz, M. Lenes, H. Brine and H. J. Bolink, *Rsc. Adv.*, 2012, 2, 3335–3339.

25 M. Kaltenbrunner, M. S. White, E. D. Głowacki, T. Sekitani, T. Someya, N. S. Sarici \square ci and S. Bauer, *Nat. Commun.*, 2012, 3, 770.

26 W. Jose da Silva, H. P. Kim, A. Rashid bin Mohd Yusoff and J. Jang, *Nanoscale*, 2013, 5, 9324–9329.

27 Heliatek reported 9% efficiency tandem OPV on foil (<http://www.heliatek.com>).

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Supporting Information

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Methods

Materials

Aqueous dispersions of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS, CLEVIOS P VP Al 4083) were obtained from Heraeus Holding GmbH and used as received. poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine] (poly-TPD) was purchased from ADS Dyesource. PbI₂ was purchased from Aldrich and used as is, CH₃NH₃I was prepared similar to a previously published method¹, in brief: *CH₃NH₃I, was synthesized by reacting 21.6 ml methylamine (40%wt in water, Aldrich) and 30 ml hydroiodic acid (57 wt% in water, Aldrich) in a 250 ml round-bottomed flask at 0 °C for 2 h with stirring. The white precipitate was recovered by evaporation at 50C for 1 h. The product, methylammonium iodide (CH₃NH₃I), was dissolved in ethanol, filtered and recrystallized from diethyl ether, and dried at 60 °C in a vacuum oven for 24 h.*

Device preparation

Devices were prepared on cleaned AZO/Ag/AZO on PET substrates, by spincoating a thin layer of PEDOT:PSS from the commercial aqueous dispersion (1200rpm 30sec and a short annealing at 150 °C result in 70 nm thickness). On top of this layer a thin film of polyTPD was deposited from a chlorobenzene solution (10 mg ml⁻¹) using spincoating. Then the substrates were transferred to a vacuum chamber integrated into an inert glovebox (MBraun, <0.1 ppm O₂ and <0.1 ppm H₂O) and evacuated to a pressure of 1 × 10⁻⁶ mbar. The sublimation of the perovskite was performed using a vacuum chamber of MBraun integrated in an inert glovebox (MBraun). Temperature controlled evaporation sources from Creaphys fitted with ceramic crucibles were employed to sublime the CH₃NH₃I and the PbI₂. The sources are directed upwards with an angle of approximately 90 ° with respect to the bottom of the evaporator. The substrates were placed at a distance of 20 cm from the top of the evaporation

sources. Shutters are present at the evaporation sources and below the substrate holder. Three quartz microbalance sensors are present in the chamber, two monitoring the rate of each evaporation source and a third one at the height of the substrate holder. After the ceramic crucibles were loaded with the $\text{CH}_3\text{NH}_3\text{I}$ and the PbI_2 the chamber was evacuated to a base pressure of 1×10^{-6} mbar. Fresh $\text{CH}_3\text{NH}_3\text{I}$ was used for each evaporation. After the base pressure was reached, the $\text{CH}_3\text{NH}_3\text{I}$ crucible was heated to 70°C . At this temperature, all three quartz sensors gave a signal. We were, however, unable to calibrate the sensor by measuring the thickness of a deposited $\text{CH}_3\text{NH}_3\text{I}$ film. Therefore, an alternative process was used. Upon stabilization of the sensor reading the crucible containing the PbI_2 was heated. Only at PbI_2 evaporation temperatures in excess of 200°C were dark brown films obtained. The film thickness of the perovskite film was monitored using quartz sensor nr 3 (at the height of the substrate holder). Perovskite films were prepared at different PbI_2 evaporation temperatures, increasing with 10 degrees from the predetermined 200°C . In this way the optimum films were obtained at an evaporation temperature of the PbI_2 crucible of 250°C . The PCBM layer was deposited using a chlorobenzene solution of 10 mg ml^{-1} in ambient conditions using a meniscus coater and a coating speed of 10 mm/second . The device was completed by the thermal evaporation of the top metal electrode under a base pressure of 2×10^{-6} mbar to a thickness of 100 nm . The solar cells (active area of 0.12 cm^2) were characterized inside the inert glovebox.

Characterization

GIXRD data were collected at room temperature in the 2θ range $5\text{--}50^\circ$ on an Empyrean PANalytical powder diffractometer, using $\text{Cu K}\alpha 1$ radiation. Typically four repeated measurements were collected and merged into a single diffractogram. Pawley refinements², were performed using the TOPAS computer program³ and revealed an excellent fit to a one-phase model with a tetragonal cell ($a = 8.80(2)$, $c = 12.57(2)$ Å) and space group $I4/mcm$. Additional peaks corresponding to the ITO substrate were also observed.

Scanning Electron Microscopy

Film thickness was investigated using a high-resolution scanning electron microscope (MERLIN, Zeiss) and micrographs were acquired using an in-lens secondary electron detector. Prior to analysis, the sample was coated with 12 nm carbon to minimize the charging effect.

Device characterization

Solar cells were illuminated by a white light halogen lamp in combination with interference filters for the EQE and J-V measurements (MiniSun simulator by ECN the Netherlands). A black mask was used to limit the active area of the device. Before each measurement, the exact light intensity was determined using a calibrated Si reference diode. An estimation of the short-circuit current density (J_{sc}) under standard test conditions was calculated by convolving the EQE spectrum with the AM1.5G reference spectrum, using the premise of a linear dependence of J_{sc} on light intensity. Current-voltage (J-V) characteristics were measured using a Keithley 2400 source measure unit. All characterization was done in a nitrogen filled glove box ($<0.1\text{ ppm O}_2$ and $<0.1\text{ ppm H}_2\text{O}$) without exposure to ambient atmosphere.

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1. L. Etgar, P. Gao, Z. Xue, Q. Peng, A. K. Chandiran, B. Liu, M. K. Nazeeruddin and M. Grätzel, *Journal of the American Chemical Society*, 2012, **134**, 17396-17399.
2. G. S. Pawley, *J. Appl. Cryst.*, 1981, **14**, 357-361.
3. Coelho, A. A. TOPAS-Academic, Version 4.1, 2007, see: [http:// www.topas-academic.net](http://www.topas-academic.net).