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A large area (70 cm²) monolithic perovskite solar module with a high efficiency and stability†

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Monolithic perovskite modules with active areas of 31 cm² and 70 cm² and with power conversion efficiencies (PCE) of 10.46% and 10.74%, respectively, were fabricated using scalable printing processes. An ambient stability of more than 2000 h with less than a 5% reduction in efficiency is demonstrated. The electrical quality of the mesoscopic hole transporter and its facilitation of efficient infiltration is paramount.

In recent years, organic–inorganic metal halide perovskites, in particular methyl-ammonium lead iodide (CH₃NH₃PbI₃), have emerged as very promising light harvesting materials for high performance and low cost photovoltaic technologies.^{1–3} Ever since the report of an efficient solid state photovoltaic device using perovskite as a light absorber with a PCE of 39%,² the growth in efficiencies has been unprecedentedly rapid, and a certified PCE of 22.1% has recently been achieved.⁴ However, these efficiencies are noted in laboratory scale devices with an active area smaller than 1 cm², produced using fabrication techniques such as spin coating and vacuum deposition. Perovskite solar cells (PSCs) are typically fabricated using costly organic hole conductors (e.g. Spiro-OMeTAD) and electrodes (Gold or Silver), and are also limited by their short-term stability.^{5–7} Scant efforts have been taken for the scale-up of these solar cells to realize market entry^{8–21} with 1 cm² device areas being quoted as “large area devices”. Work done on large area PSCs (41 cm²) has been summarized in Table S1 (ESI†)

Broader context

Perovskite solar cell (PSC) technology has shown unprecedented gains in efficiency, increasing from 3.8% in 2009 to its present day level of 22.1%. Beyond its high performance, PSC also promises a low cost manufacture due to the simple fabrication techniques utilized in its production. However, these kinds of high efficiencies are only recorded using small devices (0.1 cm²). In this study, we demonstrate the upscaling of perovskite solar modules with a high efficiency and stability using solution based processing and low cost electrode materials. Monolithic perovskite modules of size 10 cm × 10 cm (active area 70 cm²) with a 10.74% efficiency, along with an outstanding shelf life stability, are demonstrated here. Fabrication of these upscaled PSC was carried out using a screen-printed process along with infiltration of the perovskite solution. The highly scalable and efficient nature of the printed large area PSCs presented here, combined with the low processing costs, will pave the way to perovskite solar cell commercialization.

with only one instance of 100 cm² area devices reported (4.3% – uncertified). Schmidt et al. demonstrated the first perovskite solar cell fabricated entirely using roll-2-roll (R2R) printing and coating techniques, using carbon or silver as the final electrode.²² However, the performance of this device dropped to 4.9% as compared to the 9.4% efficiency obtained for small area devices fabricated using standard laboratory techniques such as spin coating and evaporation of the electrodes.

The successful translation of the perovskite solar cell technology relies on the development of large area, mass produced, stable devices fabricated under ambient conditions. Thus commercialization requires concurrent development of materials, device architectures and fabrication processes. Recent reports have suggested that mesoscopic carbon, which can play the role of the hole transport and electrode, could yield high efficiencies and advantages in air stability.^{5,23–29} Herein we report the fabrication of carbon based stable large area monolithic perovskite solar modules (PSMs) with an active area of 70 cm². These modules were fabricated using a facile semi-automated screen printing process, which can be tuned according to industrial needs. The large area cells showed a PCE of 11%

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with an excellent stability over 2000 h under ambient conditions. The fabrication process is highly reproducible, as the efficiency of eighteen modules fabricated in one batch, showed a standard deviation of 0.1%, which is promising for perovskite translational efforts. To the best of our knowledge, this is the first report on the development of such a large area high efficiency, stability and monolithic perovskite solar module.

Since the primary intention was to surmount the technological barriers for perovskite solar cells, all trials were performed on substrates with a 50 cm² area. In this work, we utilised a screen printer (Fig. S1a, ESI†) that can print on a maximum substrate size of 10 cm × 10 cm. Screens (Fig. S1b, ESI†) were designed to utilize a maximum substrate area for an active device while avoiding shorting between adjacent strips. The gap between the two strips is measured from the trailing edge of the carbon layer of the first strip and the leading edge of the TiO₂ of the next strip and was fixed at 3 mm for the 5 cm × 10 cm substrate (Fig. S1b, ESI†). Each strip of the active area has a width of 7.75 mm and length of 10 cm resulting in a total active area of 31 cm², which is 460% of the total substrate.

Fig. 1 illustrates the layer by layer architecture of a mesoscopic carbon based perovskite module. Fig. 2d and e show cross sectional scanning electron microscopy (SEM) images of the device with and without perovskite, respectively. The optimum thickness of the different layers required for achieving the best performance are 500 ± 50 nm for meso-TiO₂, 1.4 ± 0.1 micron for ZrO₂ and 10–12 micron for carbon. In Fig. 2e, it can be clearly seen that perovskite has homogenously infiltrated different mesoporous layers. The large perovskite crystals (thickness 4.1 μm, Fig. 2e) observed at the ZrO₂/carbon interface would have less recombination hence enhancing the open circuit voltage V_{oc}. Fig. S2 (ESI†) shows the optical image of the backside of PSM for two different cases of meso-TiO₂ pores filling with perovskite. The dark regions in the image (Fig. S2b, ESI†) indicate fully infiltrated regions, while the lighter regions are only partially filled (Fig. S2a, ESI†). Poor pore filling of the perovskite can lead to increased recombination and series resistance.

As mentioned previously, the quality of mesoscopic carbon has a significant impact on the performance. Three different types of carbon paste were used to make the 31 cm² PSM. Carbon 1 and 2 were made by mixing graphite and carbon

Fig. 2 (a) SEM image of three different carbons; (b) current density vs. voltage curve under AM 1.5G illumination (100 mW cm⁻²) of the device; (c) BET surface and resistivity; cross sectional SEM of the devices (d) without perovskite and (e) with perovskite embedded in the various layers.

nano-particles (less than 500 nm particle size) in a 75 : 25 weight ratio, while varying the amount of ethyl cellulose (binder) and terpineol to form a good dispersion. The reduced amount of binder used in carbon 2 enhanced the conductivity of the film. The details of carbon paste preparation are described in the ESI† Carbon 3 was provided by DYESOL, Australia. The Current density–voltage (J–V) curves of PSMs with different mesoscopic carbon are shown in Fig. 2b and the photovoltaic data are summarized in Table 1. From the photovoltaic data it is clear that module performance is highly dependent on the carbon layer characteristics. PSMs fabricated with carbon 3 show the highest efficiency of 10.03%, whereas carbon 1 shows a PCE of only 2.85%. To explain this difference in the performance, various characterizations (four probe conductivity, Brunauer–Emmett–Teller (BET) and SEM) were performed on the carbon films. The results of resistance measurements using a four-probe method, and surface area using a BET method, are shown in Fig. 2c. The surface morphology is shown in the SEM images in Fig. 2a. A higher magnification image is available in the ESI† Fig. S3.

Table 1 Summary of the material's properties and device parameters for different types of carbon devices

Device type	Carbon film property		Device performance			
	BET surface area (m ² g ⁻¹)	Resistance (Ω sq ⁻¹)	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE _{max} (%)
Carbon 1	9.42	40.21	7.70	3.65	40.52	2.85
Carbon 2	12.21	15.32	17.90	3.51	41.1	6.23
Carbon 3	67.32	8.47	18.83	3.69	57.66	10.03

^a Current density (J_{sc}) of a single strip.

Fig. 1 Schematic diagram of the perovskite solar module. Dimensions specified for 5 cm × 10 cm modules.

Fig. 3 (a) Process flow of module fabrication using screen printing for modules; (b) infiltration and crystallization step for perovskite: STEP 1 – resting at room temperature for 60 minutes, allowing perovskite solution to infiltrate through all of the device stack; STEP 2 – annealing at 50 °C for 90 minutes, slow formation of perovskite crystals starting from meso-TiO₂; STEP-3 – annealing at 60 °C for 30 minutes, to ensure full formation of the perovskite crystals.

Compared with carbon 1 and carbon 2, carbon 3 has a dense and homogenous distribution of carbon particles which may lead to a high surface area and better interfacial properties.³⁰ Low resistance of the carbon film is important for a charge transport and a high surface area is required for perovskite solution dripping inside the mesoporous structure of TiO₂ and ZrO₂. Fig. S4 (ESI†) shows a cross section SEM image of a full module with all three carbons. The module with carbon 3 (Fig. S4c, ESI†) shows complete perovskite filling, which can be attributed to the high BET surface area (67.32 m² gm⁻¹, Fig. 2c). The modules with carbon 1 (Fig. S4a, ESI†) and carbon 2 (Fig. S4b, ESI†) show incomplete and non-uniform pore filling, which can be attributed to the low BET surface area (9.42 m² gm⁻¹, Fig. 2c), and hence has a poor performance.

After choosing carbon 3 as the layer of interest, the fabrication of the PSMs was carefully optimized. Fig. 3 shows the detailed process flow for the fabrication of PSM. The PSM fabrication process is divided into two steps: (1) screen printing of electrode layers (Fig. 3a) and (2) the introduction of perovskite into the mesoporous layers through the carbon (Fig. 3b).

Screen printing is an easily scalable process, which can be transferred from a rigid glass substrate to continuous roll-to-roll (R2R) processing with a minimal change in processing parameters. In the next generation design (substrate size 10 cm × 10 cm) an active area of 70 cm² was achieved by reducing the gap between two strips to 1 mm (Fig. S1b, ESI†). Due to high positioning accuracy (±10 mm) of the screen printer it was possible to decrease the gap between the strips to 1 mm. Each strip width was decreased to 7 mm to optimize the drop casting process and perovskite infiltration in ZrO₂ and meso-TiO₂. It is important to keep each perovskite drop size and drop timing optimum to achieve maximum pore filling of ZrO₂ and meso-TiO₂. Fluid displacement within pores depends on a large number of parameters, including the wettability and the relative affinity of the fluids to the solid. It has been shown that increasing the wettability of the infiltration fluid promotes pore filling that stabilizes the infiltration, and weakens as the flow

rate increases and viscous instabilities become dominant.³¹ The infiltration depth and the filling fraction (i.e. volume fraction of the pores filled by the perovskite) are important parameters of pore filling. In addition to the established roles of the carbon, viz., (1) to act as a hole transporting layer, (2) to serve as a top electrode and (3) as protection from the humid environment for high stability, the infiltration of perovskite in the device also depends on the quality of the carbon layer. This will be discussed in greater detail below.

Another critical step for optimum pore filling and perovskite crystal formation is the heat treatment process. This step is very crucial because it helps to improve the quality of various interfaces (carbon/ZrO₂ and ZrO₂/TiO₂), which may reduce charge recombination at the interface. Perovskite solution infiltration and the sintering process was divided into four steps as shown in Fig. 3b. For each strip drop casting is carried out slowly and it is important to keep the droplet size optimal for the perovskite solution to flow in the pore structures of the carbon layer. In our case the optimum drop volume was 1.5 ml. Also the release time and location of consecutive droplets are critical. Perovskite droplet can either penetrate through the thickness of the film or spread across the surface and not infiltrate deep inside the device structure. The detailed studies about spreading and sorption of liquid in pores indicate that the droplet size, pore size, surface area and viscosity are important.^{32,33}

Each strip required around 25–30 ml of solution for complete wetting, which leads to better pore filling. The available surface area of carbon plays a major role in the capillary flow throughout the device structure. We attempted to infiltrate the perovskite solution from the sides of the printed structure using the capillary force of micropore structures to fill the meso-TiO₂ and ZrO₂. This approach does not work efficiently since the horizontal diffusion of solution from the dispensing end to the opposite end dominates the capillary action. After dropping the precursor on all strips, the substrate is left on a flat surface for sixty minutes. This step ensures that the pores in ZrO₂ and meso-TiO₂ are optimally filled. It has been observed that perovskite solution starts to overflow from the side wall of the device, if the holding time is increased for too long. The two step heating process is used for *g*-butyrolactone (GBL) solvent evaporation and perovskite crystal formation (Fig. 3b). Heating is carried out at 50 °C for 90 minutes for slow drying of the film. The mild temperatures used reduces the possibility of solvent trapping inside the device structure due to rapid perovskite formation. Once the solvent evaporation is completed, the heating temperature is increased to 60 °C. The substrate is kept at this temperature for 30 minutes for further perovskite crystallisation.

The current–density–voltage (J–V) characteristics of the PSM of area 5 cm × 10 cm and 10 cm × 10 cm are shown in Fig. 4 and summarized in Table 2. All measurements were performed under standard reporting conditions (AM 1.5G) without any encapsulation. Both the PSM showed impressive PCEs over 10%. One of our 5 cm × 10 cm devices was tested in an accredited PV test laboratory (Newport Corporation PV Lab,

Fig. 4 Current density vs. voltage curve under AM 1.5G illumination (100 mW cm^{-2}) (a) $10 \text{ cm} \times 10 \text{ cm}$ device (active area 70 cm^2); (b) $10 \text{ cm} \times 5 \text{ cm}$ device (active area 31 cm^2); image of (c) $10 \text{ cm} \times 10 \text{ cm}$ device and (d) $10 \text{ cm} \times 5 \text{ cm}$ device.

Table 2 Summary of device parameters; open circuit voltage (V_{oc}), current density (J_{sc}) of a single strip, fill factor (FF) and efficiency (η)

Device area (cm^2)	Scan type	J_{sc} (mA cm^{-2} strip)	V_{oc} (V)	FF (%)	PCE_{max} (%)	P_{max} (mW)
70	Reverse	17.72	9.63	62.9	10.75	752
	Forward	17.97	9.29	60.49	10.10	707
31	Reverse	19.6	3.72	57.5	10.46	315
	Forward	19.58	3.63	57.3	10.19	306

Bozeman, USA), which certified a PCE of 9.11%, with J_{sc} of 20.96 mA cm^{-2} , V_{oc} of 3.766 V and a FF of 0.47 (Fig. S5, ESI†).

It was observed that the fill factor (FF) for the larger module with an active area of 70 cm^2 is higher than that of the smaller module with an active area of 31 cm^2 . The 70 cm^2 module has a smaller interconnect width of 1 mm as compared to the 3 mm width of the 31 cm^2 module. As the travelling distance is reduced between interconnects, this reduces the amount of series resistance contributed by FTO, hence improving the fill factor of the 70 cm^2 device. The strips in the module are series connected, resulting in the adding up of the V_{oc} 's and the smallest J_{sc} of the strip fixing the total current of the module. The J_{sc} in the smaller module is higher than the larger module due to the larger strip width in the smaller module. The V_{oc}/cell in the larger module is higher than the smaller module, because the smaller module has a larger strip width and strip area, which may lead to more recombination, hence decreasing the V_{oc}/cell . Also, the increased width of the smaller module also results in higher series resistances, contributing to the reduction of V_{oc} .

The maximum power (P_{max}) is a critical characteristic of any photovoltaic module. P_{max} for a $5 \text{ cm} \times 10 \text{ cm}$ module is 315 mW and for a $10 \text{ cm} \times 10 \text{ cm}$ module is 752 mW .

Fig. 5 (a) PCE of 18 modules made in one batch and (b) PCE of module with time.

To check the reproducibility of performance, 18 modules of $5 \text{ cm} \times 10 \text{ cm}$ were fabricated and tested. The photovoltaic performances of these modules are shown in Fig. 5a. The statistical distribution of the photovoltaic parameters (V_{oc} , J_{sc} , FF and PCE) along with P_{max} is summarized in Table S2 (ESI†). The standard deviation for photocurrent conversion efficiency is less than 1% and for P_{max} is 29.07 mW , which are less than 10% of the best module. Similarly, V_{oc} , J_{sc} and FF show standard deviations of 1.56 mA cm^{-2} , 0.14 V and 0.94% , respectively. All the photovoltaic parameters show a standard deviation that is less than $\pm 8\%$. This confirms that the whole fabrication process is highly reproducible. The I-V characteristics of the module were measured over a period of 84 days under ambient conditions (Fig. 5b).

The change in efficiency over a period of more than 2000 h is less than 5% (relative). This suggests that the devices are quite stable under ambient conditions (65–70% RH and 25–30 °C). Steady state measurements were performed by biasing a module close to the maximum power point under illumination for 72 hours. Beyond an initial setting time (05 minutes) the perovskite module is extremely stable. IV measurements conducted before and after the stability tests show an almost invariant response (Fig. S6, ESI†). The high stability of the module can be attributed to the top carbon layer which is hydrophobic and hence prevent moisture related degradation of the perovskite crystals (Fig. 6).

To further elucidate the difference in the performances of the devices with carbon, photoluminescence (PL) and time

Fig. 6 (a) Photo luminescence (PL) spectra; (b) time-resolved PL (TRPL) measurements of the full device. The samples were excited with 100 fs, 1 kHz, 600 nm laser pulses (0.1 mJ cm^{-2}).

resolved photoluminescence (TRPL) measurements were performed on the best and worst carbon layers. Samples were excited with 100 fs, 1 kHz, 600 nm laser pulses (0.1 mJ cm^{-2}). Due to the thickness of the ZrO_2 layer (1.4 μm), the PL signal primarily originates from perovskite embedded within the ZrO_2 layer. The luminescence gives an indication of the perovskite crystal quality (defect concentration, crystal size). The highest luminescence and longest lifetime are observed for the carbon 3 layers. The lower defect concentration for the perovskite within the ZrO_2 ensures that the charge transport within the ZrO_2 layer is more efficient. However, since no modification of the ZrO_2 was performed across the 3 samples, it is puzzling to observe a higher quality of perovskite within one. A more reasonable explanation could be related to the filling fraction of perovskite within ZrO_2 . A poorer filling of the perovskite within ZrO_2 would mean that a higher fraction of the PL signal originates from the perovskite at the ZrO_2 /carbon interface. Carbon can quench the luminescence efficiently and create the fluctuation in the PL signatures between the two samples. The poorer filling for carbon 1 was confirmed by cross-sectional imaging of the full device (Fig. S4, ESI†).

Conclusions

In summary, we have reported a facile and cost effective approach for the fabrication of large scale area perovskite solar modules. The modules showed impressive PCEs close to 11% and showed excellent long term stabilities (2000 h) under ambient conditions. The reproducibility of the modules was excellent (8 devices having a PCE standard deviation of only 0.65%). The critical role of carbon in the determination of the efficiency of the device is highlighted. In addition to low electrical resistance, hydrophobicity, the mesoscopic carbon layer critically determines the perovskite filling fraction of the ZrO_2 and TiO_2 layers.

Conflict of interest

The authors (A. Priyadarshi, L. J. Haur, S. Kulkarni, G. Xing, T. C. Sum, N. Mathews, S. G. Mhaisalkar) of the manuscript certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript. The authors (P. Murray, and D. Fu) are employees of Dyesol Ltd and certify that they also have no conflict of interest (financial or non-financial) in the subject matter or materials discussed in this manuscript.

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