

## SCALABLE MANUFACTURING OF MULTIPLE CATION PEROVSKITE SOLAR MODULES

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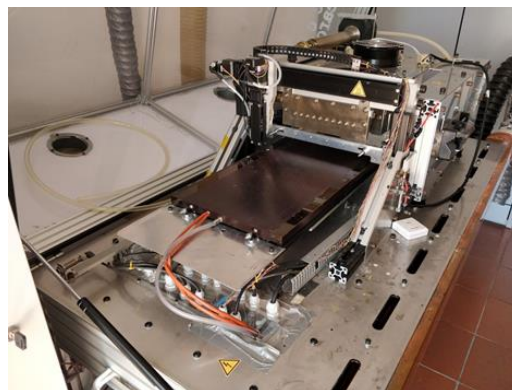
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**ABSTRACT:** In the last decade, perovskite solar cell (PSC) technology showed an efficiency improvement from 9.7% to 25.2% approaching the Si record of more than 26%. The low-cost perspective of PSCs is achievable only if scalable processes in manufacturing conditions such as pilot line or plant factory are designed and optimized for the full device stack. Here, we demonstrate a semi-automatic and scalable solvent quenching/doublestep method, based on the blade-coating technique, to deposit the triple cation perovskite in ambient air on module size. We assess the homogeneity of the perovskite layer and of the full stack by scanning electron microscopy images and profilometry measurements. Moreover, we compared the efficiency of modules fabricated by different deposition procedures: blade-coating in ambient air, spin-coating in nitrogen air and ambient air. In the first case the efficiency was about 16%, while the spin-coating technique exhibited efficiencies about 15% and 13% in nitrogen and ambient air, respectively.

**Keywords:** perovskite, module manufacturing, PV module, blade coating

### 1 INTRODUCTION

The comparable fabrication procedures with organic electronics, dye-sensitized and copper indium gallium selenide solar cells pushed the performance of perovskite (PVSK) solar cell technology till 25.2% [1–5]. The perovskite for photovoltaic technology is formed by an organic/inorganic cation as methylammonium  $\text{CH}_3\text{NH}_3^+$ , formamidinium  $\text{CH}(\text{NH}_2)_2^+$ , Cs or a mixture of them, a divalent IV-A group metal (usually lead) and an inorganic halide anion (I-, Br- or Cl-). The triple cation perovskite (CsMAFA) mixture pushes the device efficiency thanks to the MAFA compound and suppresses the yellow phases impurities thanks to Cs [6]. The maximum efficiency in literature on small area cell is 23.5% by adding a passivation interlayer between the perovskite and the HTM (hole transporting material) to reduce interfacial defects [7]. Generally, the CsMAFA perovskite is deposited in nitrogen glovebox environment at room temperature by spin coating technique with a solvent (chlorobenzene) quenching process [8]. The described process shows some issues for the perovskite technology upscaling route: i) the spin coating technique cannot be considered a scalable deposition method if the aperture area of the device increases [9]; ii) the process is strongly dependent to the user and needs intense manual practice [8]. Moreover, the reference process reported in literature is realized in a nitrogen-filled glove box that is not replicable in a real plant [10]. Based on our knowledge, very few papers reported triple cation small area cells in ambient air by ink-jet printing, blade or meniscus coating with efficiency of 20% [10–13], whilst the fabrication of modules based on stable triple cation perovskite by using scalable coating technique in ambient air without any dipping step is lacking. In this work we show an efficient CsMAFA perovskite module (11 cm<sup>2</sup> aperture area) fabricated in ambient air by adopting a semi-automatic air-assisted blade coating machine (Fig. 1) in a double step quenching method.

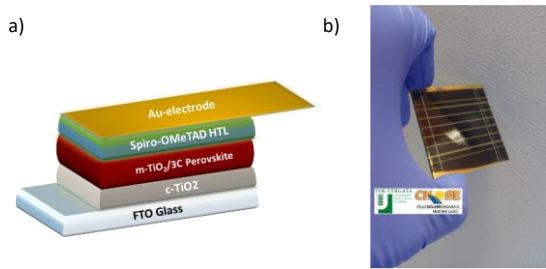


**Figure 1:** Blade coater assembled by Cicci Research in collaboration with the Centre for Hybrid and Organic Solar Energy (Tor Vergata University of Rome).

We demonstrate the deposition homogeneity by scanning electron microscopy images and profilometry measurements. Finally, we compare three deposition procedures, blade-coating in ambient air and spin-coating both in ambient and nitrogen air, in terms of module efficiency. We have not the chance to test the nitrogen air/blade condition, because the machine we used has a big size (more than 1 m<sup>3</sup>) since it is designed for large scale production (Fig. 1).

### 2 MATERIALS AND METHODS

We adopted the mesoscopic n-i-p structure (Fig. 2a).



**Figure 2:** a) n-i-p cell stack. b) perovskite solar module fabricated.

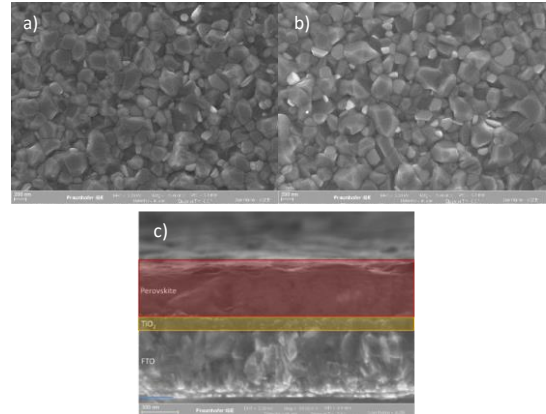
The process to realize the blade-coated module on a  $5.6 \times 5.6 \text{ cm}^2$  substrate is as follows [14]. Fluorine-doped tin oxide (FTO)-glass substrates are patterned (P1) by a nanosecond UV raster scanning laser ( $\lambda=355 \text{ nm}$ , Nd:YVO<sub>4</sub> pulsed at 80 kHz) [15]. We deposit the c-TiO<sub>2</sub> by spray-pyrolysis technique and the diluted mp-TiO<sub>2</sub> ink by blade-coating or spin-coating technique and then sintered at 480 °C for 30 min. The CsMAFA 3C perovskite ((Cs<sub>0.05</sub>(MA<sub>0.17</sub>FA<sub>0.83</sub>)<sub>0.95</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub> in DMF/DMSO) is deposited by blade coating (ambient air, 30% RH) and spin coating (glove box and ambient air environment) techniques. The blade coating deposition process is assisted by a controlled and heated airflow to pre-dry and smooths the perovskite surface. The solvent quenching step is with 2-propanol by blade-coating technique. Blading and drying systems are placed at a precise distance from each other and can be controlled via software by the user. The blade speed for the two steps (10 and 20 mm/s) and the perovskite solution concentration (1.2 M) play a crucial role in the optimization process. The spin-coating in nitrogen air parameters are 1000 rpm, 5 s ramp up, 10 s then 5000 rpm, 2s ramp up, 30 s. Then, we add chlorobenzene 7 s before ending. In both cases, blade and spin, the modules are annealed at 100 °C for 40 min. The ambient air/spin module is fabricated by following the protocol from Singh et al. [12]. The HTL Spiro-OMeTAD solution (Borum 60 mM in chlorobenzene; the molar ratio between the dopants and the Spiro-OMeTAD was 0.5, 3.3, and 0.03 for lithium bis(trifluoromethanesulfonyl)imide, 4-tert-butylpyridine, and cobalt additive, respectively) is coated by blade-coating and spin-coating (nitrogen air) methods. The next step is the removal (laser P2) of the full stack (ETL/mp-TiO<sub>2</sub>/PVSK/HTL) deposited on FTO from the vertical connection areas to series connect two adjacent cells with the subsequent electrode deposition. Then, 90 nm thick Au counter-electrode is thermally evaporated in a high vacuum chamber. Finally, the counter electrode P3 laser ablation permits the electrical insulation between adjacent cells. The patterned modules show 5 series connected cells with a total active area of 10 cm<sup>2</sup> (Fig. 2b).

The morphological analysis is realized with a field emission scanning electron microscope (Auriga 60 workstation, Zeiss) equipped with a patented Gemini electron gun. Acceleration voltage was set to 5 kV, the working distance was approx. 5 mm. An in-lens detector was used for image generation. The photovoltaic characteristics are measured with a class A sun simulator (Sun 2000, Abet) at AM 1.5 1000W/m<sup>2</sup> calibrated with an SKS 1110 sensor (Skye Instruments Ltd., Llandrindod Wells, UK); the system is equipped with a 2612 source meter (Keithley Instruments Inc., Cleveland, OH, USA)

and a LabVIEW interface.

### 3 RESULTS AND DISCUSSIONS

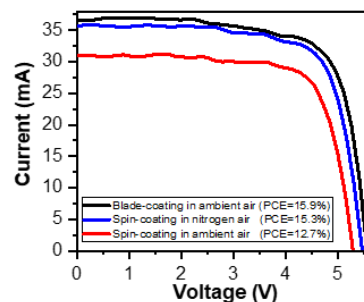
We realized top view SEM images of the bladed samples (Figs. 3a, b) at the beginning and at the end of the substrates to testify the homogeneity of the perovskite deposition by blade-coating technique.



**Figure 3:** Perovskite layer a) at the beginning and b) at the end of the coating process. c) SEM cross section.

The images reveal the same morphology and grain size distribution at beginning and end of the coating area, indicating a homogeneous coating of the whole module substrate. The grain size was found to be about 200 nm and the perovskite thickness in different spots of the deposition was about 490 nm, being in accordance with the CsMAFA perovskite in literature [6,8]. The SEM cross section (Fig. 3c) shows the perovskite grains avoid stacking on top of each other resulting in high charge transport and FF of the devices.

We compared the reported fabrication procedure in ambient air with the procedure based on the spin-coating technique both in nitrogen and in ambient air (Fig. 4).



**Figure 4:** IV curves of modules fabricated by different fabrication procedures: blade-coating in ambient air, spin coating in nitrogen and ambient air.

The scalable technique reached an efficiency of 15.9%, about 5% more than the spin-coated module in nitrogen air and 20% the spin-coated module in ambient air. The reproducibility of the proposed method is about 2% respect to 10% of the spin coating method. The compared methods have different performance because the bladed samples reveal smaller defects in respect to the spinned samples. The spin-coated device in ambient air has mainly a lower density current respect to the reference glove box condition. We believe that further investigations about spin coating conditions out of glove

box and solvent optimization are required, but it goes beyond the scope of the present work that focuses on the identification of a scalable coating technique in ambient air. Moreover, the optimized blade-coating procedure has about 70% less material consumption respect to the spin-coating technique.

#### 4 CONCLUSIONS

In few years, perovskite solar cell got efficiency closed to the silicon technology. The scaling up from small area cells to modules is the development step for any Photovoltaic technology<sup>[16]</sup>. The large area modules manufacturing process should be low cost, reliable and high throughput, with good performance and stability of the devices<sup>[17]</sup>. One of the advantages of the perovskite technology is the possibility to use the well-known and cheap printing/coating techniques<sup>[3]</sup>. The CsMAFA perovskite entered in between the different perovskite compositions as a possible way to have efficient and stable devices<sup>[6]</sup>. In literature many researchers reported several methods to upscale the technology<sup>[18]</sup>, but no one demonstrated the feasibility of efficient triple cation perovskite module in ambient air by using scalable technique for both perovskite and antisolvent. In this work we showed a process based on the air-assisted blade-coating technique in a double step quenching method. The module efficiency at 1SUN illumination is about 16%, 15.3% and 12.7% for blade-coated in ambient air, spin-coated in nitrogen air and spin-coated in ambient air devices, respectively. Further characterizations about failure analysis and stability are in progress.

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