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# Slot-die processing of flexible perovskite solar cells in ambient conditions

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ABSTRACT

Hybrid organic/inorganic perovskite materials have become promising candidates for photovoltaic applications. Typically, lab-scale perovskite devices are fabricated by spin coating under inert atmosphere conditions (inert gases and low relative humidity) which is incompatible with scaling-up processing. In this paper, we report the fabrication of perovskite solar cells in ambient conditions (average 65% relative humidity) and low temperature, by using a slot-die technique in a Mini Roll coater. A detailed optimization of the deposition parameters for the constituent layers in a flexible and planar perovskite solar cell is discussed. In particular, the resulting layers morphology strongly depended upon the processing temperature. The optimized device architecture reached a power conversion efficiency up to 2.9% with good reproducibility and reporting forward and reverse performance. The obtained results suggest that the slot-die processing of flexible hybrid perovskite solar cells at ambient conditions can be achieved with significantly reduced production costs and reliable and scalable technology.



## 1. Introduction

Inorganic-organic halide perovskite solar cells have recently emerged as a promising photovoltaic technology. Their advantageous features include the implementation of earth-abundant materials and potential low-cost processing (Ball et al., 2013; Burschka et al., 2013; Espinosa et al., 2015; Green et al., 2014; Kazim et al., 2014; Xiao et al., 2014) making them a strong candidate for future high-efficiency solar cells. Surprisingly, their photoconversion efficiencies (PCE) have increased from 3.8% (Kojima et al., 2009) to 22.1% (N.C. For, 2016) in the last six years reaching the efficiency level obtained by silicon solar cells. Nevertheless, the breakthroughs in perovskite solar devices have been primarily achieved in small lab-scale conditions with controlled atmosphere using thin film deposition techniques such as spin coating (Jeon et al., 2015), physical vapor deposition (Liu et al., 2013) and including thermal annealing at relatively high sintering temperature (Jeon et al., 2014). Such a device processing is incompatible with large-scale manufacture due to the high production costs involved. This limitation can be overcome by implementing compatible roll-to-roll processes such as slot-die (Schmidt et al., 2015) and doctor blade (Deng et al., 2015) at low temperature.

Moreover, mainly fluorine-doped tin oxide (FTO) or indium tin oxide (ITO) coated glass substrates are typically used for fabrication of perovskite solar cells. Although these substrates represent the state of the art in semitransparent electrodes, there are several concerns regarding their high rigidity, weight and frangibility, which limits the potential integration of solar devices into roll-to-roll processing on a large scale (Gupta et al., 2014; Roldan-Carmona et al., 2014). A direct solution to this problem is the implementation of flexible substrates. In fact, besides enhancing the processability of solar cells, the mechanical flexibility enable innovative energy products based on the device resulting in low thickness, lightweight, integration and portability (Chu et al., 2010; Fan and Javey, 2008; Galagan et al., 2011; Guha, 1998; Lee et al., 2008; Yoon et al., 2008). As a reference, Tables S1 and S2 present the state-of-the-art for different perovskite solar cells developed on flexible substrates using conventional lab-scale processing methods or printing techniques, respectively. Among printing methods compatible with roll-to-roll process, slot-die coating has achieved the greatest success in large-scale production of photovoltaic devices. This technique produces a uniform strip with sharp edges, which is required in the design of the film. Through this process, different film thicknesses can be easily obtained by controlling the solution properties. Another advantage of this coating process is that there is not loss of raw materials since all the injected solution is transferred to the substrate (Hong et al., 2013; Krebs, 2009). So far, for a flexible solar cell with

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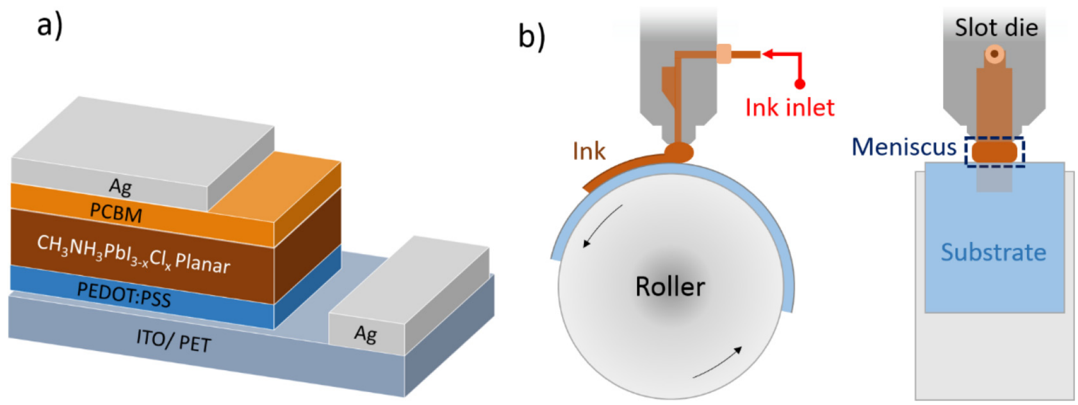


**Fig. 1.** Device configuration optimized in this study and processing technique used to obtain its constituent films. (a) p-i-n planar architecture. (b) Scheme of slot-die coating in a roller. Under this technique the coating process takes place when a meniscus is formed between a slot-die and a substrate (typically polymeric) adjusted in a roller under movement and heated or at room temperature. Here, the ink that will form the film is supplied through the inlet in the slot-die by an automated syringe, which controls the pump rate of the ink towards substrate.

all semiconducting layers deposited by slot-die, a champion efficiency reaching 5.1% average PCE has been reported (Gu et al., 2015; Schmidt et al., 2015). However, these results were achieved by applying a monolayer (C3-SAM) on a poly (3,4- ethylenedioxy thiophene):poly(styrenesulfonate) (PEDOT:PSS) hole transport layer (HTL) to modify the crystallinity and bilayer of electron transporters (ETL) as PCBM and ZnO. Additionally, it does not specify the processing relative humidity, which, as well known, plays an important role in the processing of the perovskite solar cells.

Here, we show highly reproducible devices manufactured by roll-to-roll process fabricated under 65% relative humidity. In this work we report the optimization layer by layer of the solar cell structure PET/ITO/PEDOT:PSS/$MAPbI_{3-x}Cl_x$/PCBM/Ag as illustrated in Fig. 1a. All constituent interlayers, except for the Ag top electrode, were prepared *via* slot-die coating (Fig. 1b) in ambient conditions at low temperature. These were optimized enabling the preparation of high-quality films. In particular, the effect of the processing temperature of the different films was carefully investigated and monitored. The temperature of the perovskite precursor was particularly relevant in order to obtain homogeneous well-crystallized films at high relative humidity (65%). At the end, the optimized processing conditions enabled devices fabricated at low temperature, high relative humidity and good reproducibility, reaching a champion 2.9% PCE in both forward and reverse directions.

## 2. Methods

### 2.1. Materials

4083 PEDOT:PSS is Clevious PVP Al 4083 from Heraeus. ITO-glass slides from Luminescence Technology. $PbCl_2$ (99.98%, Merck Chemicals) and $CH_3NH_3I$ (dyesol) mixed with mole ratio of 1:3 were dissolved in dimethyl formamide in a concentration of 20, 33 and 40%. The precursor solution was stirred at 60 °C for 3 h inside in ambient conditions. Prior to slot-die coating, the solutions were filtered using 0.45 μm PTFE syringe filter. PC60BM (99.5%, Merck Chemicals) was dissolved in chlorobenzene with a concentration of 20 mg/mL and stirred at 60 °C for 4 h and filtered before use. Silver wire (99.9% sigma – Aldrich).

### 2.2. Device fabrication

The patterned ITO-PET substrates were cleaned with water and isopropanol. On cleaned ITO substrate, a layer of PEDOT:PSS (Clevios PVP AI 4083 added 1/3 isopropanol by volume) was deposited by slot-die coating in a FOM technologies mini roller at web speed of 0.5 m/min, followed by heating at a temperature of 50 °C and annealed at 120 °C for 20 min. The resulting films presented different thickness dependence on the pump rate solution. A peristaltic pump included in the mini roller set up allow controlling the pump rate. A thickness of 58 nm with a pump rate of 0.6 mL/min was found to be optimal. Afterwards, the precursor the perovskite was deposited by slot-die on PEDOT:PSS layer at web speed of 0.5 m/min with different concentrations (20, 33 and 40%) varying the pump rate and controlling the ramp annealing. This resulted in 311 and 49 nm optimal thick and roughness film, respectively, using a concentration of 33%, a pump rate of 2.5 mL/min, an application temperature of 80 °C and a crystallization ramp as follows: 80 °C by 40 min, 90 °C by 10 min, 100 °C by 10 min and 110 °C by 20 min. A layer of PCBM was slot-die coated on the perovskite film with different pump rates (0.01, 0.015, 0.02, 0.03, 0.05 and 0.08) mL/min, a web speed of 0.5 m/min, an application temperature of 60 °C and annealing temperature of 100 °C during 20 min. An optimal thickness of 62 nm with a pump rate of 0.15 mL/min was achieved. 130 nm-thick Ag was evaporated on the PC60BM layer through a shadow mask under a vacuum of $10^{-6}$ torr. Further experiments are required in order to optimize a silver paste in order to fully solution process the devices.

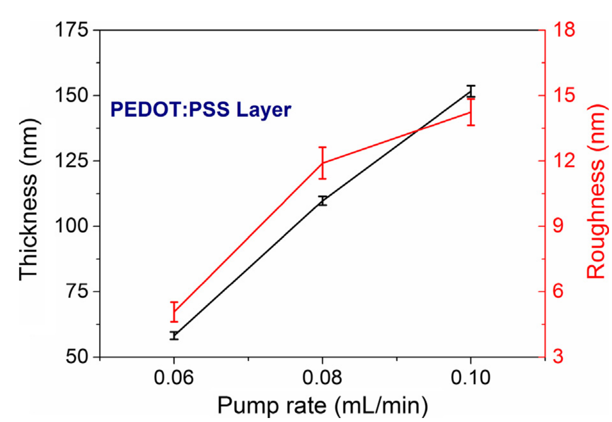


**Fig. 2.** Dependence of thickness and roughness with the pump rate for PEDOT:PSS thin films on top of ITO-coated PET.