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Aqueous-Processed Perovskite Solar Cells Based on Reactive Inkjet Printing

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We report a one-step method for aqueous-processed perovskite active layer via reactive inkjet printing (RIJ) technique. The perovskite was successfully applied to fabricate solar cell devices. This is to the best of our knowledge, the first time that the RIJ technique is demonstrated in the fabrication of perovskite solar cells.

I. INTRODUCTION

Perovskite solar cells have been extensively developed in the recent five years due to their high efficiency, solution processability and low-cost [1-5]. Notably, the rapid progress of perovskite solar cells in terms of power conversion efficiencies (PCEs) has already approached a comparable level of traditional polycrystalline silicon solar cells [6]. Hence, there is a need for manufacturing techniques to bring this academic frontier to industrial applications. The fabrication of such highly efficient solar cells typically contains a mesoporous metal oxide (*e.g.*, TiO_2 or ZrO_2) layer to facilitate the electron transport [7]. However, the mesoporous layer requires high a temperature sintering process, slowing down the production and increasing the manufacturing cost. Recently, planar heterojunction (PHJ) perovskite solar cells have shown high PCEs without the need for a metal oxide layer [8,9]. These PHJ devices have a similar layout as organic photovoltaics and inherently feature high flexibility and low-temperature processability [10,11]. Such devices demonstrate the possibility of roll-to-roll (R2R) fabrication of perovskite solar cells.

Inkjet printing is a R2R compatible technology and has been applied mainly as a deposition tool in organic electronics [12-15]. Currently, spin coating [16], drop casting [17], and dip coating [18] are the dominant approaches for active layer fabrication of perovskite solar cells on laboratory scale. However, these methods are not compatible with large-scale manufacture. Inkjet printing offers a low-cost approach where functional materials are deposited only on desired areas [19]. Besides direct patterning capability, the scalability and reproducibility features of inkjet printing have made the technique an attractive scaffold to develop the manufacturing process of solar cells [20]. Very recently, inkjet printing was introduced to the fabrication of perovskite solar cells. In one example, Song and coworkers used inkjet printing to deposit the perovskite precursor mixture (CH_3NH_3I and PbI_2) on a mesoscopic TiO_2 film to prepare the perovskite layer [21]. A PHJ perovskite solar cell was also demonstrated on spin-coated PbI_2 surfaces by inkjet printing, employing CH_3NH_3I and carbon black mixture as the ink material [22]. There are still lingering issues with inkjet printing of perovskite solar cells. A common problem is the clogging of the nozzle [23] arising from the poor solubility of the materials in solvents suitable for inkjet printing. Moreover precursor materials for fabricating perovskites have a good solubility in limited choice of solvents such as typically *N*,*N*-dimethylformamide (DMF)], while are not preferred solvents for large scale manufacturing process [24,25]. To overcome these drawbacks, we chose to combine water-soluble perovskite precursors with reactive inkjet printing (RIJ) technique [26]. RIJ has been previously applied to prepare metallic materials [27], polymers [28] and nanoparticles [29]. The technique allows the *in situ*

synthesis of functional materials at specific locations on the substrates, simplifying the fabrication process [30]. During the RIJ process, reactive inks (reactants) are separately deposited on the same spot. Thus the reaction between the precursors proceed after the inkject printing and not within the nozzle, thus avoiding any nozzle clogging issues if the product precipitates [31]. Herein, we report a one-step method for aqueous-processed perovskite active layer *via* reactive inkjet printing technique. In this strategy, we used a multichannel inkjet printer to separately deposit lead(II) acetate trihydrate [$Pb(OAc)_2 \cdot 3H_2O$] and methylamonium iodide (CH_3NH_3I) on the same spot of solid substrates (Figure 1a). $Pb(OAc)_2$ and CH_3NH_3I aqueous solutions were used as reactive inks to form the perovskite layer. The perovskite formation was further confirmed by structural characterizations and successfully applied to perovskite solar cell devices. This is to the best of our knowledge, the first time that the RIJ technique is demonstrated in the fabrication of perovskite solar cells.

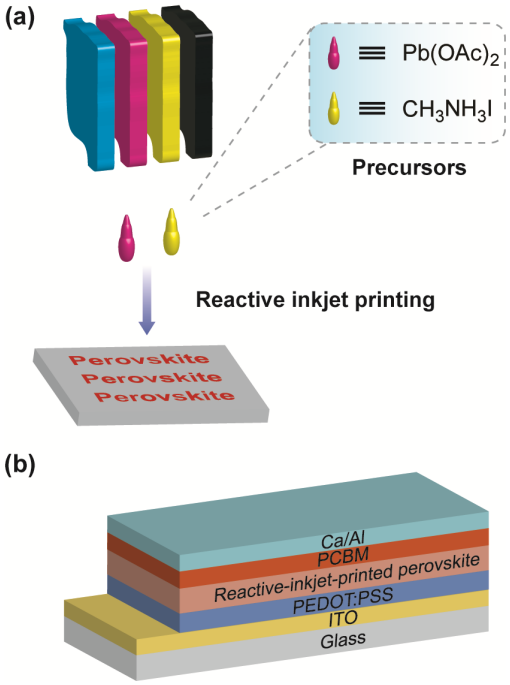

Figure 1. (a) Schematic illustration of the fabrication of perovskite material using reactive inkjet printing technique. (b) Schematic illustration of the solar cell structure.

II. METHOD

Lead(II) acetate was purchased from Sigma-Aldrich Co. LLC. Methylammonium iodide was purchased from 1-Material Inc. Isopropanol (99.9%) was purchased from Fisher Scientific. All the materials were used without further purification. Water was obtained from *Mili-Q* system.

For our studies, we used an Epson Artisan 50 Inkjet Printer as the multichannel printer model. The printer has been demonstrated with a precise CMYK-based control in previous reports [32,33]. $Pb(OAc)_2$ ink was prepared at a concentration of 60 $mg \cdot mL^{-1}$ and loaded into the magenta channel as the lead source. CH_3NH_3I ink was prepared at a concentration of 90 $mg \cdot mL^{-1}$ and loaded into the yellow channel as the organic cation source. The solvent for both of the reactive inks was a mixture of water and isopropanol (v/v = 1:1). Other channels were loaded with blank solution (water or isopropanol). The color combination was set at a 1 to 1 mixture of magenta and yellow so that the molar ratio of two precursors were approximately kept at 1:3 [$Pb(OAc)_2$ to CH_3NH_3I] [34,35]. The reactive RIJ was carried out at ambient conditions with a five-minute annealing at 100 °C after the printing process. The printed patterns are shown in Figure 2.

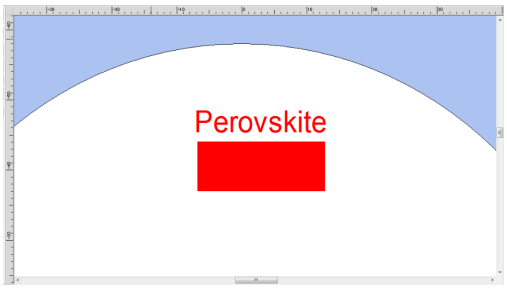

Figure 2: Screenshot of designed pattern for fabricating RIJ-processed perovskite layers.

The perovskite layer was characterized using scanning electron microscopy (SEM), powder X-ray diffraction (PXRD) and atomic force microscopy (AFM). The SEM was operated on a Magellan 400L XHR-SEM with an accelerating voltage of 2.0 kV and currents of 13−25 pA. The inkjet-printed $Pb(OAc)_2$ film was pretreated with 40-s gold coating to get focused images. PXRD

were measured using a PANalytic X'Pert[3] X-ray diffractometer having a Ni filter, 1/2 in. diverging slit, vertical goniometer, and X'Celerator detector. Samples on glass slides were scanned from 2θ = 5°−60° under Cu K*a* (1.542 Å). AFM was carried out using an Asylum Research MFP-3D-SA AFM with samples printed on silicon wafers.
Pre-cleaned ITO substrates were treated with UV/O_3 (UVO Cleaner, Model 342, Jelight Company, Inc.) for 15 minutes. Subsequently, a layer of PEDOT:PSS was spin-coated at 3000 rpm for 60 seconds (G3P-8 Spin Coater, SCS) after filtering through a 0.45-µm PVDF filter (Millex, EMD Milipore) under ambient conditions. The resulting substrates were then annealed in air for 30 min at 150 °C and cooled down to room temperature. The annealed coated substrates were then applied to UV/O_3 treatment for 3 minutes. The RIJ of reactive inks was carried out afterwards. Next, a solution of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) was prepared in chlorobenzene at a concentration of 20 $mg{\cdot}mL^{-1}$ and then spin coated on the as-printed substrates at 1000 rpm for 60 seconds. Afterwards, Ca and Al was thermally deposited at a pressure of 1×10^{-6} mbar (Figure 1b).

III. RESULTS

From the optical images (Figure 3), a distinct color change from yellow to brown was observed after the 5-min thermal annealing of RIJ film, indicating perovskite formation. From the SEM images (Figure 4), we can clearly observe the crystallization resulted from the RIJ process compared to the individually printed inks. The perovskite crystals ranged from 1 to 2 µm. AFM results revealed a wire-like morphology of the RIJ-perovskites. (Figure 5).

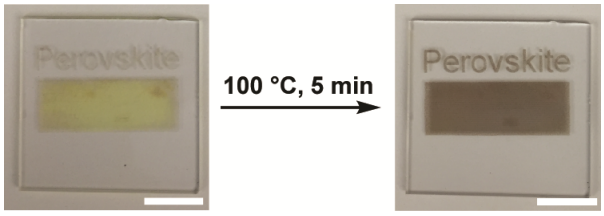

Figure 3. Optical images of as-printed film and the perovskite conversion after thermal annealing. The white scale bar is 5 mm.

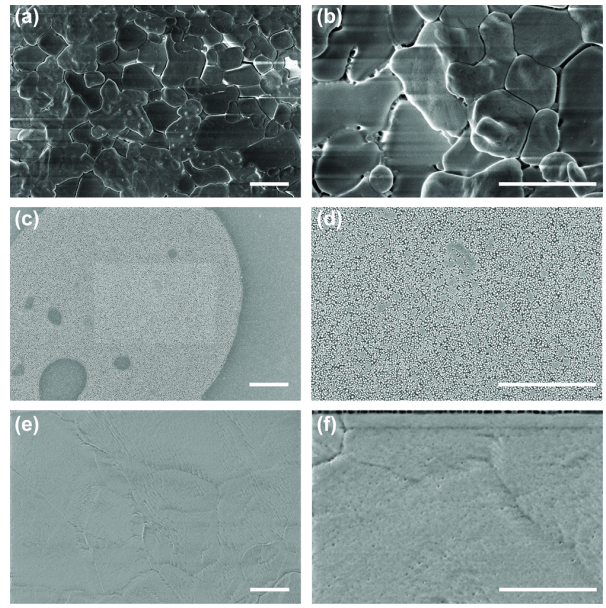

Figure 4. Scanning electron microscope images of (a), (b) RIJ-processed film; (c), (d) inkjet-printed $Pb(OAc)_2$ film; (e), (f) inkjet-printed CH_3NH_3I film. The white scale bar is 1 µm.

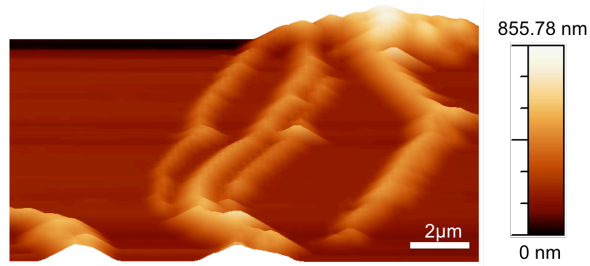

Figure 5. 3-D Tapping mode AFM image of RIJ-perovskite film revealing a wire-like morphology.

Further structural analysis on the RIJ-processed perovskite layer was obtained from PXRD results. A complete conversion of $Pb(OAc)_2$ was observed, however there has presence of iodoplumbate complexes [36] observed (2θ = 11.4°) in the blue trace in Figure 6. There is a large peak at 2θ = 13.9° which is attributable to the (101) tetragonal $CH_3NH_3PbI_3$ (*I4cm*) phase.

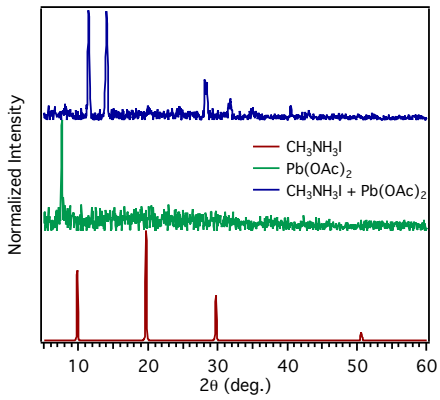

Figure 6. Powder XRD spectra of reactive inkjet printing-processed perovskite and inkjet-printed precursors.

Finally, we measured the device efficiency containing the RIJ-processed perovskite material as the active layer. The measurement was done under AM1.5G solar simulator at 100 mW·cm^{-2} light intensity with a scan rate of 250 mV·s^{-1}. A high reproducibility was observed from the device performance. The best device with a RIJ-processed perovskite layer showed V_{oc} = 0.50 V, J_{sc} = 4.28 mA·cm^{-2}, FF = 44.4% and PCE = 0.94% (Figure 7a), showing a successful fabrication approach to perovskite solar cells based on RIJ technique. Relatively low efficiency was observed due to very thin and non-uniform perovskite layer with wire-like morphology on PEDOT:PSS coated ITO substrate. Further, PEDOT:PSS is partially soluble in aqueous medium and could be effected during RIJ process. Therefore, further optimization such as precursor ink-formulation, ink concentration, substrate properties, surface treatment and substrate temperature is required to improve the uniformity and thickness of the film to get desired solar cell efficiency from this environmental friendly aqueous processing of RIJ technique. To compare with the conventional inkjet printing of perovskite solar cells from organic solvent, we have also fabricated perovskite active layers from N,N-dimethylformamide (DMF) solvent having maximum efficiency of 3.73% (Figure 7b) but with very low reproducibility. The major challenge faced during organic solvent based inkjet printing other than toxicity issue is the printer head clogging and damage even at room temperature. Choice of hole or electron transport layer (it should not get dissolved in aqueous medium but is compatible to solution processing such as NiO_x [37] or CuO [38]) would therefore be very important to fabricate uniform pin-hole free perovskite active layer from RIJ technique. It is also compatible to combinatorial screening of organic cations during film formation [33].

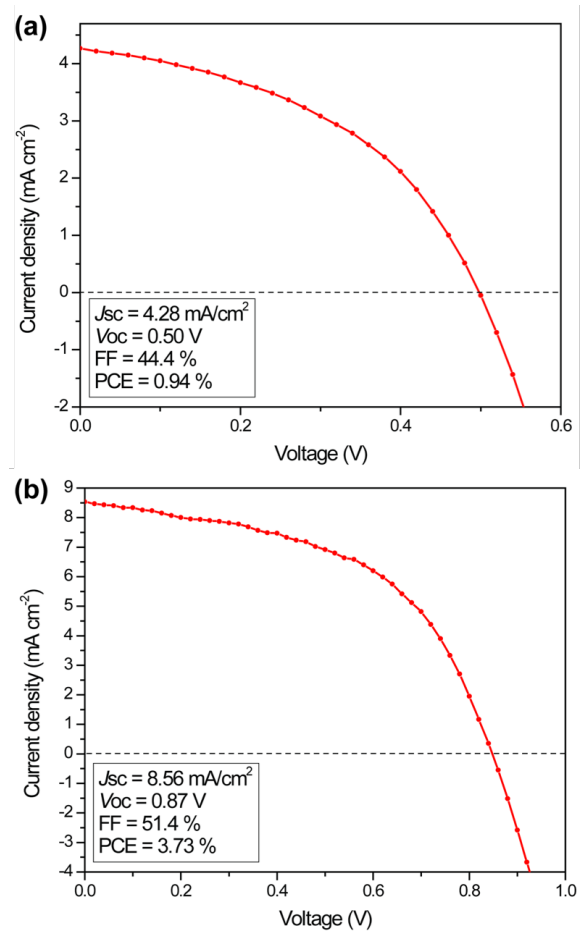

Figure 7. Current-voltage curve of a perovskite solar cell containing perovskite layer fabricated by (a) reactive inkjet printing; (b) sequential inkjet printing of lead(II) iodide in DMF and methylammonium iodide/formamidinium iodide in isopropanol.

IV. CONCLUSION

We have successfully demonstrated a simple and environmental friendly reactive inkjet printing approach to fabricate highly reproducible

perovskite solar cells. The perovskite material was processed using aqueous solutions of perovskite precursors from multi-channel commercial ink-jet printer at ambient condition. This method is potentially useful to facilitate a rapid screening for the optimal stoichiometry between lead source and organic cation. Moreover, it provides a R2R compatible way to fabricate perovskite solar cells.

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