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Solvent-assisted crystallization via a delayed-annealing approach for highly efficient hybrid mesoscopic/planar perovskite solar cells

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ABSTRACT

The formation of a dense and uniform perovskite film with large grain is an important factor for getting excellent device performance. Here, we report an optimized solvent-assisted crystallization procedure followed by a delayed annealing for easy and reproducible fabrications of perovskite solar cells with a hybrid mesoscopic configuration. The working electrode contains a mesoporous TiO_2 scaffold layer of 100 nm deposited on FTO substrate with a thin TiO_2 blocking layer. The devices in this study were assembled using all commercially available materials without any extensive modification. Formation of uniform and pin-hole free perovskite nanocrystals with film thickness 200 nm on top of the scaffold layer was achieved via an optimized solvent-assisted crystallization method. A much smoother perovskite layer was achieved with a delayed annealing for a certain period. The best performing device was obtained at the annealing delayed for 60 min, giving the power conversion efficiency 16.9% with an average value 15.4% obtained from 60 devices.

1. Introduction

Solution processed thin-film solar cells such as dye-sensitized solar cells [1], quantum dot solar cells [2,3], organic solar cells [4,5] and heterojunction solar cells [6] are regarded as promising alternative for development of new generation photovoltaic devices. Perovskite solar cells (PSCs) based on hybrid organometallic halide nanocrystals as light absorbers have attracted substantial attention due to their remarkable photovoltaic performance and cost-effective processing. Additionally these perovskites possess excellent optical properties [7], ambipolar charge transport [8] and sufficient electron-hole diffusion lengths [9,10]. The power conversion efficiency (PCE) of the PSCs has been rocket-boosted from less than 10% to over 20% in just three years [2,11,12]. The highest reported PCE so far is 22.1% achieved by Seok and co-workers [13]. Two major device architectures, namely mesoscopic [14–19] and planar heterojunction [20,21], have been utilized to achieve the PCEs higher than 16%. Although the planar devices have achieved greater efficiencies, the effect of hysteresis was reported to be significant in solar cells of this type [22–27]. A high contact resistance for electron transfer between perovskite layer and dense TiO_2 layer in the planar heterojunction structure is proposed to be responsible for the hysteresis [26]. Considering of this, the addition of a mesoporous TiO_2 layer would offer a lower contact resistance for forward electron transfer from the perovskite due to its higher surface area, relieving the severity of hysteresis effect in mesoscopic nanocomposite device structure. Moreover, an optimally thick mesoporous TiO_2 layer will improve the efficient charge collection from perovskite layer via the large surface area of mesoporous TiO_2 layer [16]. The formation of a dense and uniform perovskite film with large crystal size is an important factor for getting excellent device performance. In addition, the grain size and grain boundary of perovskite play a crucial role on overall device performance. For example, several groups have reported the micro-scale kinetics of perovskite films using the imaging techniques of micro-photoluminescence, micro-electroluminescence and photoconductive atomic force microscopy [28–30]. Those results show that the device performance depends on the surface morphology of the

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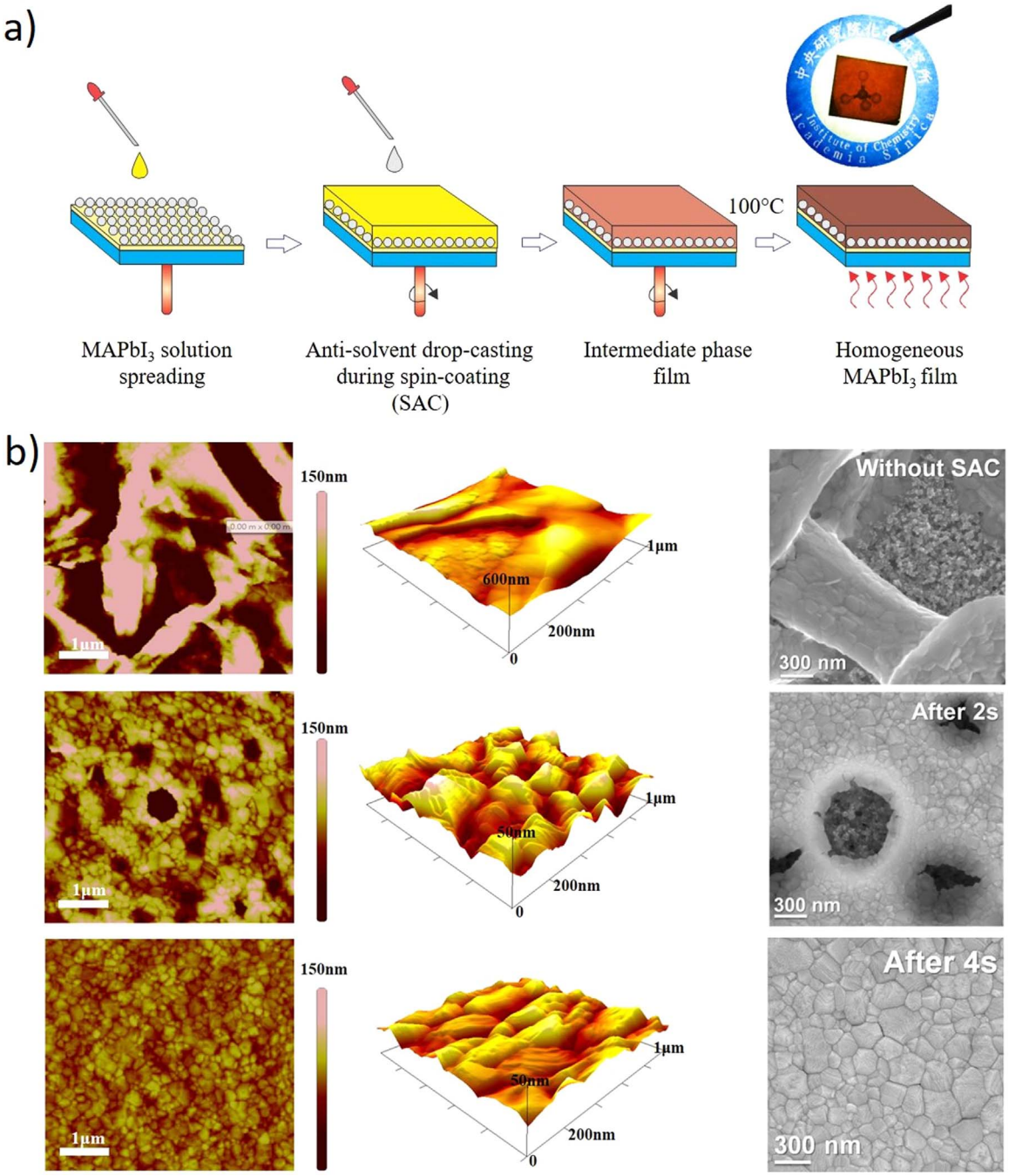

Fig. 1. a) Schematic illustration of solvent assisted crystallization method and b) AFM and SEM images of the $MAPbI_3$ surface prepared by adding chlorobenzene at different times after the start of spin-coating.

film; large grain size and less grain boundary in bulk perovskite significantly promote the efficiency of the cell.

The methylammonium lead iodide ($MAPbI_3$) perovskite layer can be prepared by several methods including one-step spin-coating method [31,32], two-step sequential deposition method [14,33] and vapour deposition method [34]. However, normal spin-coating method cannot form a homogeneous and uniform film with a large surface area. Use of an anti-solvent method during the spin coating process has been found to produce highly uniform and dense perovskite layer [16]. Jeon et al. have reported a bilayer perovskite architecture using poly(triarylamine) (PTAA) as a hole-transporting material (HTM) to obtain the highest efficiency of 16.5% and the average efficiency of approximately 15.2% calculated for over 100 devices [16]. They have utilized toluene as an anti-solvent in a two-step spin-coating method. A one-step, solvent-induced fast crystallization method also has been introduced for planar PSCs, through which highly flat and uniform $MAPbI_3$ thin films have been produced. By utilizing this faster and facile solution processing method, the optimized device showed a promising PCE 16.2% [35]. Although the reported device performance is promising, the low average efficiency and the hysteresis effect in those planar PSC devices could be a major obstacle for its widespread application.

In addition to modification of spin-coating conditions for increasing the grain size of the perovskite layer, some post-treatment methods also have been reported in order to improve the morphology of perovskite film. Post-annealing treatment using solvent vapour has been investigated by several groups [36–38]. Solvent post-annealing was first reported by Xiao et al. on p-type device configuration [36]. The solvent post-treatment was an effective method to increase the perovskite layer