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Comprehensive studies of air-brush spray deposition used in fabricating high-efficiency $CH_3NH_3PbI_3$ perovskite solar cells: Combining theories with practices

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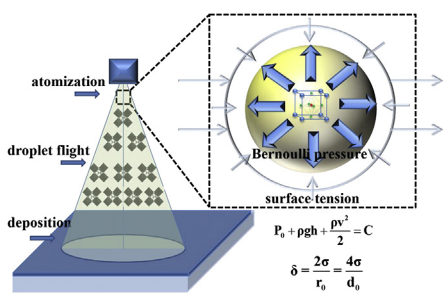
HIGHLIGHTS

- Spray coating method is explored to prepare perovskite films for large scale production.
- The spraying process is discussed from principles to parameters.
- The devices with spraying method show excellent optical and electrical properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Organic-inorganic perovskite solar cells (PSCs) are among the most attractive and efficient emerging thin film photovoltaic technologies. The perovskite films have been fabricated by lots of deposition methods, including one-step/two-step spin coating, thermal evaporation and vapor assisted processes. However, the laboratory-based fabrication methods are not well matched with large area manufacture for actual use. Spray coating deposition technique is being explored to prepare perovskite films to break the bottleneck plaguing large scale production. Herein, a comprehensive study is conducted in fabricating perovskite films by air-brush spraying method. The spraying process is classified into three stages, namely, 1) atomization process, 2) droplet flight and 3) film deposition. Each of them is discussed in detail from principles to parameters. Integrating the three aspects above, high quality perovskite films comparable to spin coated films are obtained. A best power conversion efficiency (PCE) of 16.68% is achieved for planar structure PSCs, which is prominent among the PSCs fabricated by spraying method. In addition, devices with spraying method show excellent optical and electrical properties. The principles we discuss here could be applied in the actual condition for mass production.

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1. Introduction

Organic-inorganic halide perovskites are appealing materials for novel thin film solar cells due to their outstanding photovoltaic performance and lower fabricating cost. The power conversion efficiencies (PCEs) of perovskite solar cells (PSCs) have been raised from the original 3.8% [1] to an impressive record of 22.7% [2] in the last few years, due to their high absorption coefficient, fast carrier mobility and long carrier lifetime of perovskite materials [3]. Generally, the formula of organic-inorganic halide perovskite is ABX_3. The site of A represents the organic cation ($CH_3NH_3^+$, $HC(NH_2)_2^+$), B site is the metal cation (Pb^{2+}, Sn^{2+}), and X site means the halide anion (Cl^-, Br^-, I^-). The component of $CH_3NH_3PbI_3$ is part of the most widely studied perovskite structures [1,3], and it is also the focus of our research. The PCEs of PSCs experienced explosive growth with the efforts of many outstanding researchers. Numerous milestone events, such as solvent engineering, crystal engineering, interface engineering and intramolecular exchange, have promoted the development of PSCs [4,6,8]. Up to now, most of the high efficient PSCs are based on-spin coating deposition process [3–6], which unfortunately fail to meet the requirements for mass-production [7–11]. In order to address this dilemma, several deposition techniques including spray coating [8,11–14], ink-jet printing [15,16], blade coating [17,18], slot-die coating [19] and chemical vapor deposition [20], have been utilized to fabricate PSCs with large size. Among these methods, spray coating is a mature manufacture technology in film deposition, and it was first introduced in perovskite film preparation by Lidzey et al. [8]. After years of exploration and development, several derivative approaches have been developed, such as ultrasonic spray coating [13,21], electric field assisted spray coating [12,14,22] and hand spray coating [11,23]. Spraying method could not only economize on raw materials, but also prepare uniform films with large area. The PCEs of devices prepared with spraying method have been increased from the initial 11.1% up to 18.3% in the past few years [8,11].

However, previous reports [8,12,13] only discussed the parameters of spraying perovskite with little in-depth study over the mechanism of film deposition. It is known that the quality of perovskite film was affected by many factors [8,9,22], such as spraying height, spraying rate, substrate temperature and the post deposition annealing, etc. From preceding reports [8,9,11–14], we could find that the PCEs of spraying PSCs varied even under the same condition, making it difficult for the following researchers to determine proper experimental schemes for further study. Thus, the relations of these factors with the final device performance still need to be clarified fundamentally from a deeper theoretical insight. We also discovered something in common with spraying process through consulting massive references [8,9,11–13,21,23–25]. In general, the process of spraying could be divided into three stages, which were 1) droplet atomization, 2) droplet flight and 3) film deposition. The size of droplet generated at nozzle was a crucial parameter in atomization process. During drop flight process, droplets would undergo either coalescing, spreading or receding. The distribution of droplets arrived at the substrate was mainly determined by atomization process. During film deposition process, the precursor solution dropped on the preheated substrate, and then the solvent evaporated quickly, leaving the perovskite nucleation/crystallization. Combined with the processes above, the atomization effect and the balance between solvent evaporation with perovskite crystallization rate, would be the internal factor for fabricating uniform, pinhole-free and large grain size perovskite films.

Herein, the uniform perovskite films were prepared through exploring spraying mechanism and process parameters from the three stages mentioned above. During droplet atomization process, the flow rate of carrier gas was regulated by the equilibrium of Bernoulli pressure with surface tension to obtain the appropriate atomization effect. According to the momentum, energy and mass equations of volatilization process, the distance between air-brush and substrate was adjusted, obtaining small droplets with relatively stable shapes and sizes in droplet flight process. During film deposition process, the solvent evaporation rate and perovskite crystallization rate were balanced by optimizing substrate temperature and the concentration of precursor solution. The devices with spraying process exhibited excellent optical and electrical properties, which could be applied in the actual condition for mass production.

2. Experimental

The materials, device fabrication and characterization were described in the supporting information.

3. Results and discussion

The solvent properties, such as boiling point, surface tension and viscosity, had significant impact on the spray-deposited films [11]. Considering the relatively prolonged drying time, the higher boiling point of spraying solvent could cause wet film shrinkage, which would lead to film thickness variation [11,13]. However, the droplets would dry before arriving at the substrate, when the boiling point was too low, leaving large density of pinholes on the film [25]. Surface tension reflected the mutual attraction of molecules on liquid surface, which would cause a shrink of the solution. The smaller surface tension of solution led to a better contact between the solution and substrates [13]. The solution with lower viscosity was easy to spread on the surface of substrates, which had the similar effect with surface tension. Several common solvents, such as DMF, DMSO and GBL, were used in perovskite precursor solution [4–6]. Table 1 exhibited the boiling points, surface tensions and viscosities of DMF, DMSO and GBL, respectively. It was well known that DMF had the lowest values in these indexes among them. Fig. 1 displayed the photos of contact angle between the compact TiO_2 (c-TiO_2) layers with DMF, DMSO and GBL, respectively. The lower contact angle indicated the better spreading ability of the solution on substrate. In Fig. 1, the contact angles were 7.1°, 8.7° and 10.6° for DMF, DMSO and GBL, respectively. Combining the data and analyses, DMF was chosen as the spraying solution to enhance the spreading ability of precursor solution on the substrate. The PCEs of perovskite films prepared with different spraying solution were shown in Table S1. The PSC, adopting DMF as spraying solution, exhibited the highest PCE compared with the others, which further verified the advantages of DMF.

3.1. Atomization process

Fig. 2a showed the schematic diagram of perovskite film deposited by spray coating, which was divided into three stages, namely, atomization process, droplet flight and film deposition. During atomization process [25], the carrier gas flow rate played a crucial role in the formation of finer droplets. The optimal gas flow would form tinier droplets with uniform size distribution. The precursor solution was driven by carrier gas flow, and a relative motion would appear between them. There existed Bernoulli pressure at the tangent interfaces between the liquid and airflow. The Bernoulli pressure could be calculated according to Bernoulli equation:

Table 1
The boiling point, surface tension and viscosity of DMF, DMSO and GBL at 25 °C.

	Boiling Point (°C)	Surface Tension (mN m^{-1})	Viscosity (mPa·s)
DMF	152.8	35.2	0.8
DMSO	189	43.6	2.0
GBL	204	52.3	1.7