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*ACS Appl. Mater. Interfaces*, **Just Accepted Manuscript** • DOI: 10.1021/acsami.9b01843 • Publication Date (Web): 25 Feb 2019

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# Efficient Perovskite Solar Cells Prepared by Hot Air Blowing Ultrasonic Spraying in Ambient Air

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**KEYWORDS:** ultrasonic spray coating, substrate heating, hot air blowing, perovskite solar cells, scalable atmospheric deposition

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4 **ABSTRACT :** Substrate heating is the most common method for controlling crystallization  
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6 during spray coating. However, due to poor controllability during substrate heating, the sprayed  
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8 films have variable thickness and rich pores, which limits the efficiency of the device. Here, hot  
9  
10 air blowing was applied to spray coating to promote the crystallization of perovskite films under  
11  
12 ambient conditions. Upon employing a hot air blowing method that stimulated uniformly  
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14 distributed nuclei growth, the pinhole-free and thickness-controllable perovskite film was prepared.  
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17 This enabled more reproducibly high quality perovskite films to achieve power conversion  
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19 efficiency (PCE) of 13.5% and obtain stabilized power output (SPO) of >12% in ambient  
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21 conditions.  
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## INTRODUCTION

Hybrid organic-inorganic perovskite has arisen as a revolutionary absorber material due to its excellent photoelectric properties. The PCE of perovskite solar cell (PSC) has exceeded 23% in only a few years<sup>1-8</sup>. However, the commercialization of PSC requires not only high PCE but also scalability and stability. Spin coating is the most commonly used perovskite film deposition techniques. In the spin coating process, the drying and flattening of wet films depend on the successive centripetal force generated by rotation. Unfortunately, spin coating is difficult to apply to the preparation of scalable perovskite films. This area of the substrate is always less than 10 cm, and most of the precursor ink (> 90%) was wasted in spin coating process<sup>9</sup>. Therefore, developing scalable perovskite film deposition methods and understanding the film formation mechanism are the key to improve the scalability of PSC devices.

Developing a suitable deposition strategy for expandable perovskite absorbing layer is a challenge for expanding perovskite solar cell devices. The technologies for scalable perovskite film deposition include blade coating<sup>10-12</sup>, slot-die coating<sup>13-14</sup>, meniscus coating<sup>15</sup>, spray coating<sup>16-21</sup>, inkjet printing<sup>22-23</sup>, screen printing<sup>24-25</sup> and electrodeposition<sup>26-30</sup>. Spray coating which can be easily scaled up and translated to roll-to-roll fabrication is a fascinating technology to meet the commercialization of PSCs. There are many examples of depositing compact oxide by pneumatic spraying<sup>31</sup> and ultrasonic spraying<sup>32</sup>. Ultrasonic spray coating (USC) could also be used to deposit perovskite absorbing layer<sup>19, 21</sup>. Previous works have focused on the substrate heating method<sup>17-18</sup> and the growth mechanism of perovskite films in ultrasonic spray coating<sup>16</sup>. By optimizing substrate temperature which could affect the perovskite films quality, the PSC devices with an

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4 average efficiency of  $10.6 \pm 1.1\%$  were obtained at  $75^\circ\text{C}$ <sup>17</sup>. The most efficient (18.3%) sprayed  
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6 PSC device was fabricated at  $120^\circ\text{C}$  of substrate temperature<sup>20</sup>. It is not easy to maintain the  
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8 delicate balance of solvent evaporation and crystallization speed by tuning the substrate  
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10 temperature. In the previous report of Zhu et al., PCE of 17.29% was obtained for the application  
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12 of antisolvent which is environmentally harmful<sup>33</sup>. Therefore, a more controllable method was  
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14 urgently needed to prepare dense uniform perovskite films via spraying.  
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20 Gas-assisting method (the gas was usually high-pressure inert gas) has been introduced to spin  
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22 coating<sup>34-36</sup>, but almost no ultrasonic spray coating. Here, we firstly applied a hot air blowing  
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24 method to ultrasonic spray coating under ambient conditions ( $\text{RH} < 30\%$ ). Good reproducible  
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26 pinhole-free perovskite films were prepared by hot air blowing ultrasonic spray coating (HAB-  
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28 USC) rather than substrate heating ultrasonic spray coating (SH-USC). The time and temperature  
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30 of air flow have been optimized to pursue pinhole-free perovskite films. The planer PSC devices  
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32 were achieved with PCE of 13.5% ( $0.13 \text{ cm}^2$ ) and 9.80% ( $1 \text{ cm}^2$ ). The HAB-USC PSC devices  
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34 were more efficient and stable, and the method of HAB-USC played a key role in low cost and  
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36 high throughput manufacturing of PSC devices.  
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## 43 **EXPERIMENTAL**

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45 **Materials and Solution Preparation.** The precursor solution of electron transport layer was  
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47 obtained by mixing 1 ml of tin oxide colloidal dispersion (Alfa Aesar, 15% in  $\text{H}_2\text{O}$  colloidal  
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49 dispersion) and 5 ml of deionized water and then stirring 2 hours.  
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4 The  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  precursor solution was obtained by blending  $\text{PbCl}_2$  (99.999%, Sigma-  
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6 Aldrich) and MAI (> 99.5%, Shanghai Materwin New Materials Co. Ltd.) in a molar ratio of 1:3  
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8 in anhydrous DMF.  
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11 The hole transport layer precursor solution was obtained following a recipe published  
12 elsewhere<sup>33</sup>. Spiro-OMeTAD (99.5%), Li-TFSI and FK-209 were all purchased from Shanghai  
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14 Zaofu New Material Technology Co., Ltd. 4-tBP was purchased from Sigma-Aldrich.  
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19 **Perovskite Film Deposition.** For spray coating, 450 mg/ml  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  precursor  
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21 solution was used. The perovskite precursor solution that was delivered by the Syringe Pump  
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23 (LSP01-1A, Longer Precision Pump Co., Ltd) was sprayed in ambient air by a self-built spray  
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25 system equipped with a 120 kHz nozzle (K12, Siansonic Technology Co., Ltd). The perovskite  
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27 films were prepared with the optimized ultrasonic spraying parameters: a nozzle height of 80 mm,  
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29 a flow rate of 2.0 ml/min, a substrate moving speed of 100 mm/s (driven by a stepper motor), and  
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31 a carrier gas pressure of 4.4 psi.  
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37 For conventional SH-USC, we have preheated the substrate with different temperature. To keep  
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39 the substrate at a specific temperature during the whole deposition process, we fixed the substrate  
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41 on a 10 cm × 10 cm aluminum plate which has high specific heat capacity before preheating. After  
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43 15 minutes preheated of glass substrate and aluminum plate, the substrate fixed on aluminum plate  
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45 was transferred to the spray system for spray coating. The annealing process was 30 minutes at  
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47 90°C for and 60 minutes at 100°C in ambient atmosphere.  
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53 For novel HAB-USC, the as-prepared substrate passed directly under the nozzle and then hot air  
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55 was applied to the wet film. The hot air of specific temperature was provided by digital display  
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4 hot air heat gun (DHCHG11600, DELIXI ELECTRIC). The distance between wet films and heat  
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6 gun orifice was 30 mm and the flow rate of hot air was 8 liters/sec. The temperature of hot air in  
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8 this work shown on the digital display screen of the heat gun. Thermal annealing process of  
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10 perovskite film was the same as SH-USC mentioned above.  
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14 **Solar Cell Device Fabrication.** For the rigid substrate, ITO/glass (Nippon, 10  $\Omega$ /sq) was  
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16 washed 15 min by sonication in deionized water, ethanol and acetone, respectively. The ITO-  
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18 coated glass was dealt with ultraviolet ozone (UVO) for 15 min before using after drying by N<sub>2</sub>  
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20 stream. SnO<sub>2</sub> layer was spin coated at 3000 rpm for 30 s and then annealed at 150°C for half an  
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22 hour in ambient air. Then SnO<sub>2</sub>/ITO/glass was dealt with UVO for 15 min before depositing  
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24 perovskite precursor solution.  
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30 For the flexible substrate, ITO/PEN (Pecell Technologies, Inc., 15  $\Omega$ /sq) was only cleaned 15  
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32 min by sonication in deionized water and then was further dealt with UVO treatment for 10 min  
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34 before use. The deposition and annealing process of SnO<sub>2</sub> on the flexible substrate as same as on  
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36 ITO/glass. Then the SnO<sub>2</sub>/ITO/PEN substrate was dealt with UVO treatment for 10 min before  
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38 spray coating.  
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43 Spiro-OMeTAD was deposited onto sprayed perovskite film prepared by aforementioned USC  
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45 methods at 4000 rpm for 30 s in glovebox filled with Nitrogen. Finally 80nm Au electrode was  
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47 thermal evaporated with a shadow mask (0.13 cm<sup>2</sup> and 1 cm<sup>2</sup>) to complete the devices.  
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51 **Measurements and Characterization.** The film morphology was carried out by scanning  
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53 electron microscope (JSM-7800), optical microscope (Photoelectric Technology Co. Ltd,  
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55 UMT203i) and atomic force microscope (Bruker Dimension Icon). X-ray diffraction was given by  
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4 Rigaku Smart Lab with a Cu K $\alpha$  source. *J-V* curves of the PSC cells were measured at a delay time  
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6 of 100 ms by Keithley 2611 source meter at room environment. There was no initial light soaking.  
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9 The light source was a solar simulator (Newport, 81904, USA) under the AM 1.5G (100 mW/cm<sup>2</sup>),  
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11 which was calibrated by a standard Si cell. Electrochemical impedance spectroscopy (EIS)  
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13 measurement of PSC device was carried out using the electrochemical lab (AMETEK, Versa  
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15 STAT 4). The Nyquist plots of these devices were carried out under AM 1.5G with an applied bias  
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17 voltage of 10 mV.  
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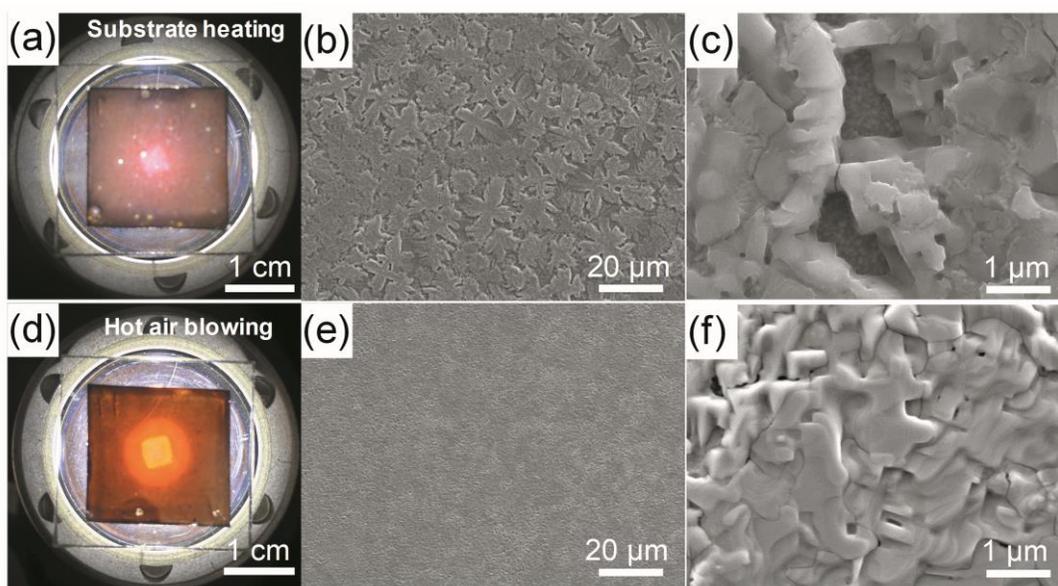
## 22 **RESULTS AND DISCUSSION**

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25 Ultrasonic spray coating had many technical parameters affecting the quality of perovskite films,  
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27 including but not limited to the height of the nozzle, the concentration and flow rates of perovskite  
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29 precursor solution, the pressure of the carrier gas and the speed of the substrate. To prepare  
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31 perovskite films with a one-step spray coating method, we have set up an ultrasonic spraying  
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33 system in our lab. The parameters mentioned above have been optimized carefully, and specific  
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35 parameters have been introduced in the experimental section. It was worth mentioning that  
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37 multiple pass spray routines could redissolve the underlying films resulting in poor quality of  
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39 perovskite films. Therefore, single pass spray routine is imperative (Figure S1).  
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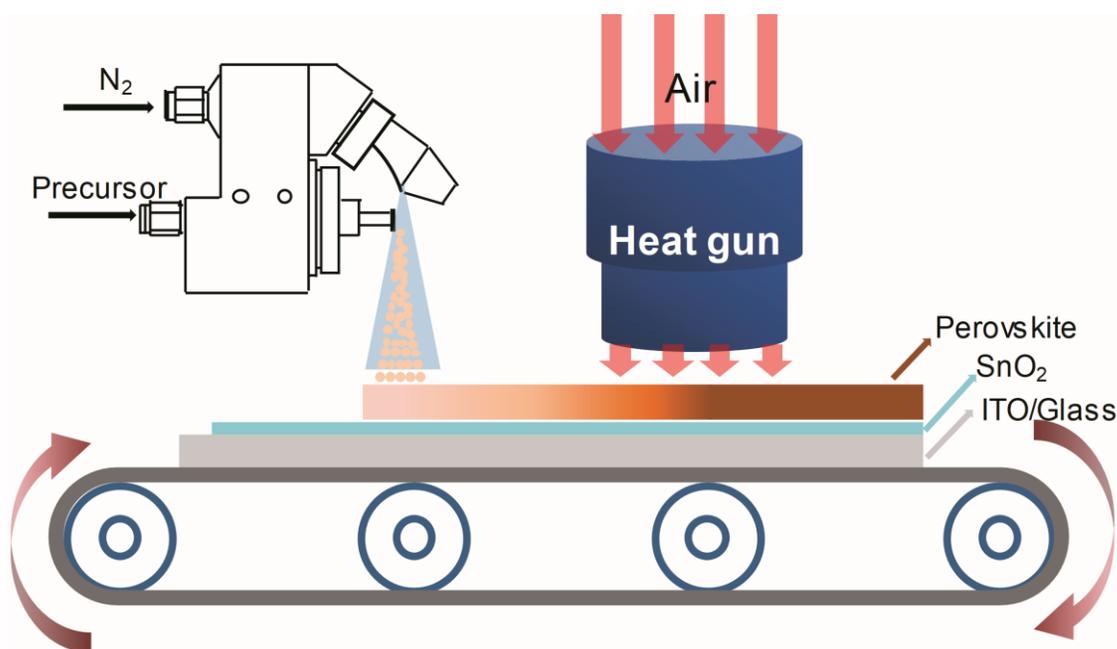
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46 The solution deposition methods of perovskite films all contain three key stages: i) the coating  
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48 of wet precursor film and coalescence of droplets, ii) the evaporation of solvent and nucleation, iii)  
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50 the crystallization of perovskite by annealing. In ultrasonic spray coating, tiny liquid droplets were  
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52 randomly dispersed onto the substrate with the assistance of carrier gas. It was easy to coat  
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54 perovskite precursor solution onto the substrate via ultrasonic spray coating, and thermal annealing  
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4 to crystallize fully the perovskite film was already a mature technology for  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  films.  
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7 The second stage of solvent evaporation was the most critical factor in the process of perovskite  
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9 film deposition. In the existing reports<sup>16-21</sup>, almost sprayed perovskite films were prepared by SH-  
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11 USC, which the solvent evaporation rate was controlled by the substrate heating method. However,  
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13 the optimized temperatures are varied in different reports<sup>16-18</sup>. We firstly prepared perovskite films  
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15 with different substrate temperature by SH-USC. Figure S2 shown that the films prepared by  
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17 relative lower temperature process exhibited irregularly distributed flower-like shaped crystal  
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19 because of the de-wetting resulted from prolonged drying time. Moreover, the films prepared by  
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21 relative higher temperature process exhibited lower film coverage and high roughness, because the  
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23 solvent evaporated too quickly to coalesce the droplets, even the solvent would vaporize  
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25 immediately upon touching the hot plate.  
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53 **Figure 1.** Digital photos and different magnification SEM images of (a-c) SH-USC perovskite  
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55 film, (d-f) HAB-USC perovskite film.  
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4 The optimal temperature was 50°C with the SH-USC method since the temperature resulted in  
5 better coverage films (Figure S2). Indeed, it was apparent that there were still relatively small holes  
6 and exposed underlying oxide (Figure 1a-c). This revealed that the high quality perovskite films  
7 and exposed underlying oxide (Figure 1a-c). This revealed that the high quality perovskite films  
8 could hardly be obtained by SH-USC. Predictably, the devices with poor coverage perovskite films  
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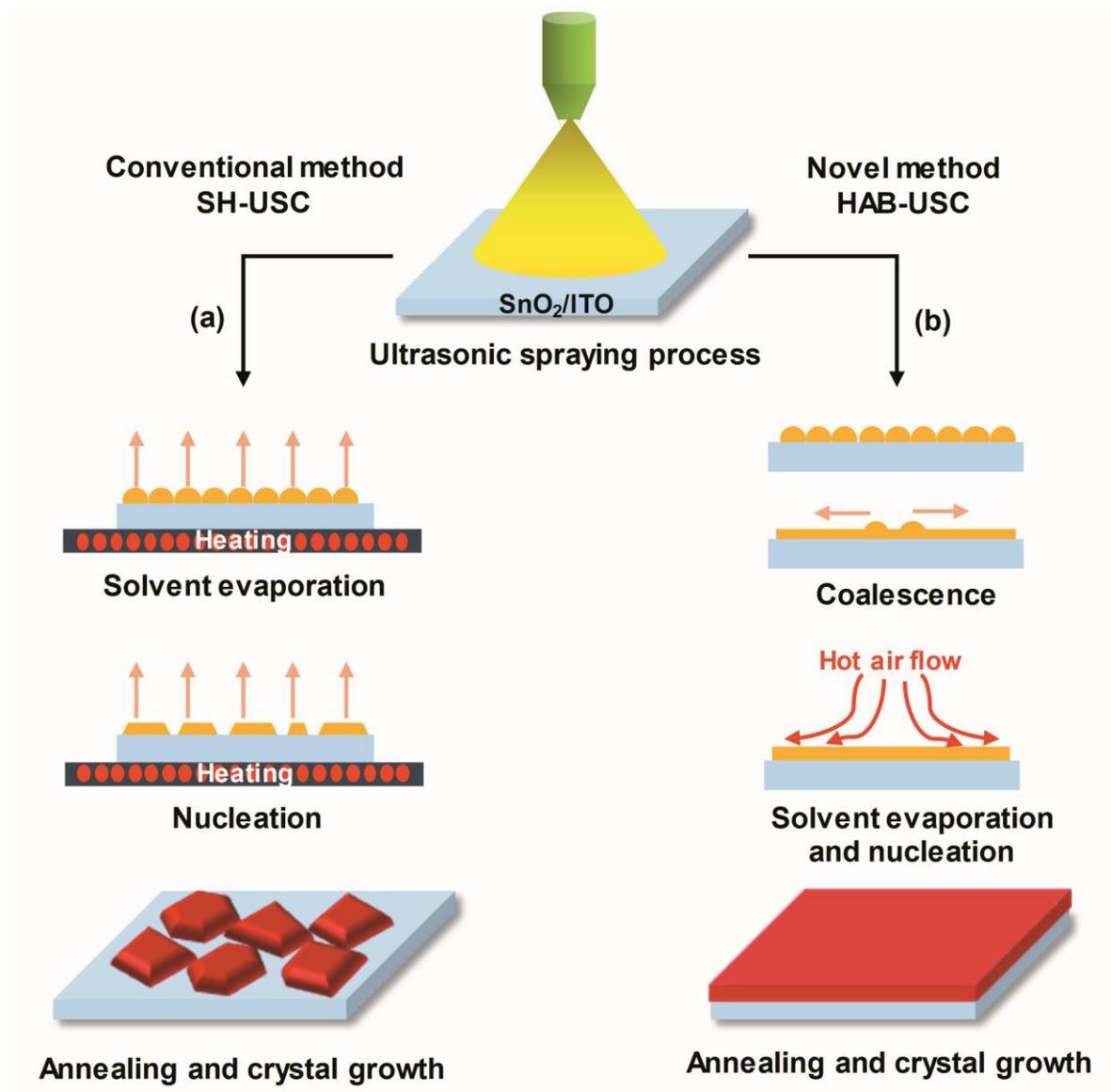
38 **Figure 2.** Schematic illustration of the HAB-USC process.

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41 For high quality perovskite films, a novel method named hot air blowing ultrasonic spray coating  
42 was developed. Figure 2 illustrated the HAB-USC process that we employed hot air blowing to  
43 deposit  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  films. The precursor ink was transported into the ultrasonic nozzle by a  
44 micro syringe pump, and broken into micron droplets by nozzle vibrating. Under the guidance of  
45 carrier gas ( $\text{N}_2$ ), a perovskite precursor wet-film was spray-coated onto the substrate of  $\text{SnO}_2/\text{ITO}$ .  
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54 To ensure the continuity of the preparation process, the substrate was driven by a stepped motor  
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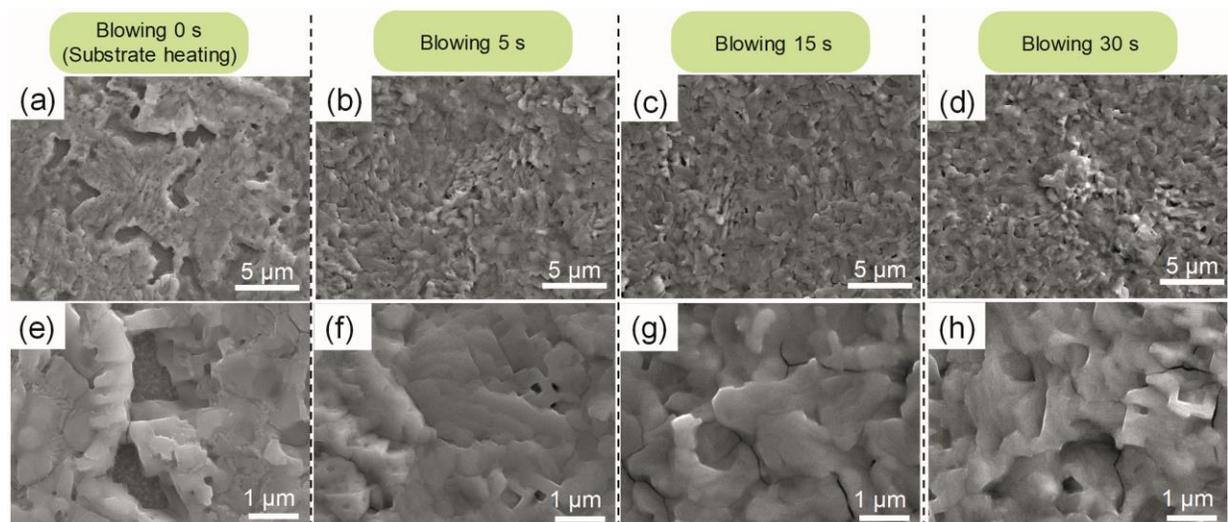
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4 to pass through directly under the ultrasonic nozzle at a speed of 100 mm/s. After a few seconds  
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6 (to ensure coalescence of droplets), hot air was used to blow the perovskite precursor wet-films to  
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8 adjust the evaporation of the solvent. It was worth mentioning that our USC system achieved  
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10 deposition speed one order of magnitude larger than blade coating (which typically was 1–13  
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12 mm/s<sup>10-12</sup>). Amazingly, upon employing hot air blowing to the preparation process of perovskite  
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14 films, pinhole-free perovskite films were obtained (Figure 1d-f). Therefore, the HAB-USC method  
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16 we have developed provided a new opportunity for obtaining high-quality perovskite films even  
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18 capturing high-efficiency devices.  
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25 As discussed above, the second stage of solvent evaporation and nucleation was the decisive  
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27 factor for high quality perovskite films. For the conventional SH-USC process, we need to increase  
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29 the temperature of the hot plate to accelerate the evaporation of solvent due to low temperature  
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31 would cause serious dewetting. When the perovskite precursor solution was just contacted with  
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33 the hot plate with higher temperature, supersaturating was formed immediately because of the fast  
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35 evaporation of the solvent. The formation of fast-supersaturated state caused rapid accumulation  
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37 of solute, resulting in uneven nucleation (Figure 3a). Therefore, the substrate-heating method could  
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39 hardly obtain perovskite films without pinholes whether it was high or low temperature, as shown  
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41 in Figure S2. However, the method of HAB-USC could promote the regulation of solvent  
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43 evaporation rate resulting in uniform nucleation by suppressing dewetting and ultrafast-  
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45 supersaturated (Figure 3b). In HAB-USC, the coalescence of micro-droplets before hot air blowing  
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47 guaranteed the full coverage of the substrate surface. Through further hot air treatment, the solvent  
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evaporated at suitable rates, resulting in evenly nucleation and finally dense perovskite films without pinholes.



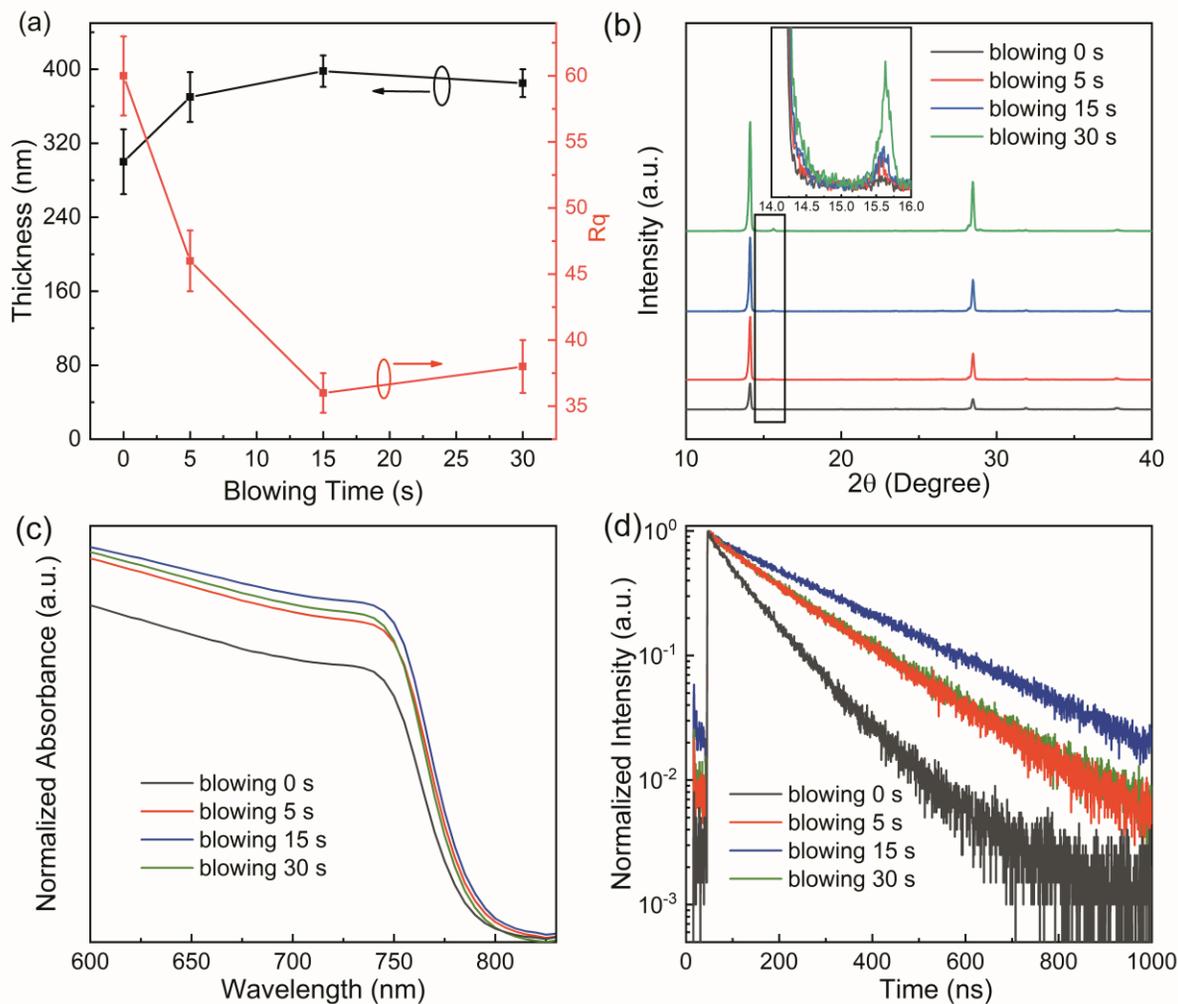
**Figure 3.** Schematic illustration of the growth of perovskite films fabricated by (a) conventional method of SH-USC and (b) novel method of HAB-USC.



**Figure 4.** (a-d) Low magnification and (e-h) high magnification SEM images of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  films with different hot air blowing time. (Especially, the film of blowing 0 s was prepared by 50°C substrate heating ultrasonic spray coating.)

To further optimize the method of HAB-USC and explore the effect of hot air blowing on the morphology of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  films, we have employed different air blowing time and temperature to deal with the perovskite wet-films. As shown in Figure S3, we achieved uniform and dense perovskite films and the optimal temperature was 120°C with blowing time of 15 s. Figure 4 shown SEM images of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  films under different hot air blowing time at 120°C. Figure S4 and S5 shown good crystallinity of all perovskite films, which could attribute to suitable post-annealing treatment and appropriate humidity (RH 20% - 30%). Exceptionally, Figure S4 shown that the films with a higher temperature ( $\geq 130^\circ\text{C}$ ) substrate heating were splitting due to the formation of smaller grain (Figure S2). As shown in Figure 4a and 4e, hole-rich perovskite films were obtained when perovskite wet-films were blown 0 s (the sample was treated with substrate heating of 50°C which is the optimized temperature of substrate heating). Especially

when hot air was applied to the wet-films, the coverage of perovskite films increased significantly even after 5 s hot air treatment.



**Figure 5.** (a) Thickness and RMS of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  films. (b) XRD patterns of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  films. (c) Absorption spectra (glass/ $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ ). (d) Time resolved photoluminescence spectroscopy (TRPL) for  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  films with different blowing time.

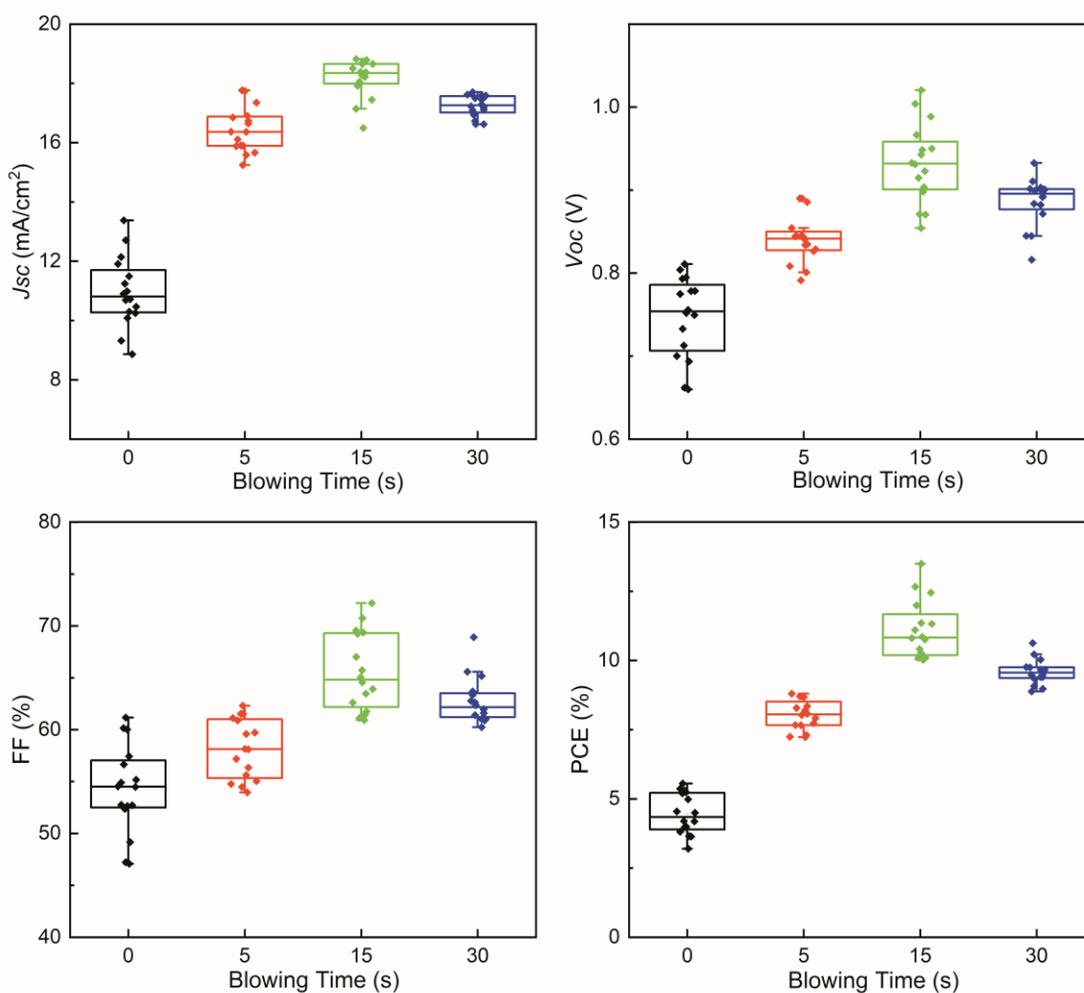
However, the perovskite films have the best morphology and optical performance when the hot air blowing time was 15 s. Figure 5a shown the roughness of the perovskite films decreased firstly

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4 and then increased as increasing the blowing time to 30 s. We made the film thickness controllable  
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6 by adjusting the precursor flow rates at a fixed substrate speed. Figure S6b shows the good liner  
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8 relationship between perovskite thickness and precursor flow rates at a fixed substrate speed of  
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10 100 mm/s. The thickness of perovskite films was measured by the step measurement method of  
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12 AFM that was introduced in Figure S7. The thickness of perovskite films with different hot air  
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14 blowing time was similar (360 nm ~ 400 nm) and apart from the sample without blowing. Figure  
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16 5b shown the films acquired sharp and strong XRD diffraction peaks. With the increase of hot air  
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18 blowing time, the intensity of the Bragg diffraction peak increased too. The molar ratio of  $\text{PbCl}_2$   
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20 and  $\text{CH}_3\text{NH}_3\text{I}$  in  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  perovskite precursor solution was pivotal to the phase purity  
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22 of annealed perovskite films. The increased blowing time of hot air led to the deviation of the  
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24 molar ratio of perovskite precursor solution because of the volatilization of organic components  
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26 ( $\text{CH}_3\text{NH}_3\text{I}$ ). The perovskite films blown 30 s exhibited increased intensity of  $\text{CH}_3\text{NH}_3\text{PbCl}_3$  peak  
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28 at  $15.6^\circ$  (the inset of Figure 5b), which would inhibit the improvement of PCE. This is consistent  
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30 with previous reports that crystalline  $\text{CH}_3\text{NH}_3\text{PbCl}_3$  would occur in annealed  $\text{CH}_3\text{NH}_3\text{PbI}_3$   
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32 perovskite films if the molar ratio of  $\text{PbCl}_2$  and  $\text{CH}_3\text{NH}_3\text{I}$  deviates from 1:3<sup>37</sup>. As shown in Figure  
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34 5c, the films blown 15 s obtained stronger absorption because of the larger thickness shown in  
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36 Figure 5a. Time resolved photoluminescence spectroscopy (TRPL) shown increased PL lifetimes  
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38 of perovskite film blown 15 s, revealing elevated film quality and reduced traps. This was essential  
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40 for high performance because of the suppression of non-radiative recombination pathways (Figure  
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42 5d).  
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**Table 1.** PV parameters of spray-coated PSCs with different hot air blowing time. <sup>a</sup>

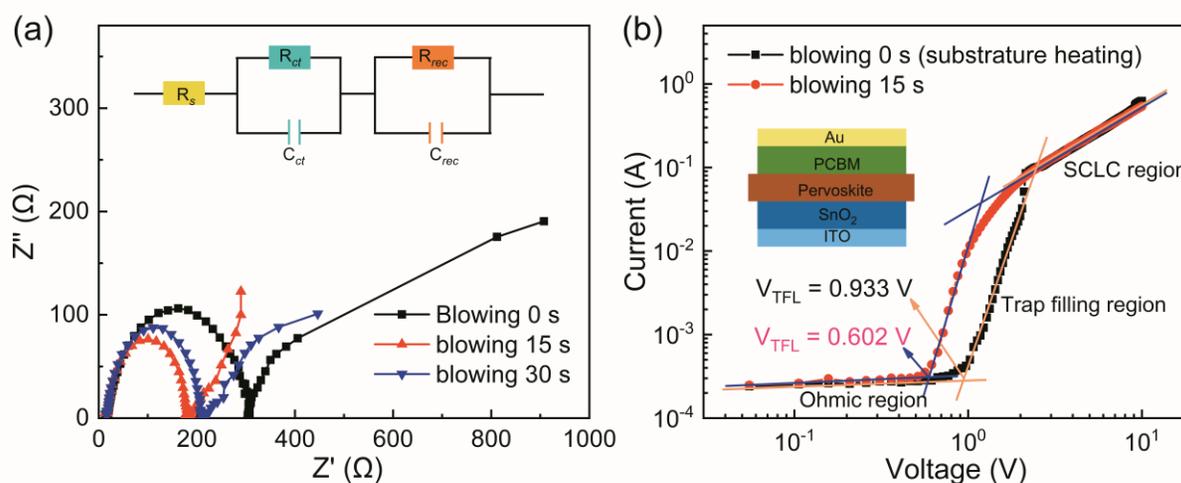
Blowing Time (s)	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF (%)	PCE (%)
0	10.97 ± 1.18	0.747 ± 0.049	54.3 ± 4.2	4.46 ± 0.73
5	16.44 ± 0.76	0.841 ± 0.029	58.2 ± 2.9	8.04 ± 0.53
15	18.17 ± 0.65	0.932 ± 0.048	65.5 ± 3.7	11.12 ± 1.05
30	17.24 ± 0.36	0.886 ± 0.029	62.8 ± 2.2	9.59 ± 0.45

<sup>a</sup> 64 cells were fabricated in four batches.



**Figure 6.** Statistical results of 64 devices in different batches treated by different hot air blowing time.

Table 1 summarized the average and standard deviation of the PV parameters of 64 devices. Figure 6 shown the device statistics of 64 devices (16 devices for each different blowing time) collected from 4 batches. With the blowing time increasing from 0 s to 15 s, all parameters had increased and  $11.12 \pm 1.05\%$  of average PCE was achieved when blowing time was 15 s. Compared with PSCs blown 15 s, these devices blown 30 s had lower  $J_{sc}$  and  $V_{oc}$  because of the impurity phase.



**Figure 7.** (a) The typical Nyquist plots of PSCs. (b) Dark  $J$ - $V$  curves of electron-only devices of hot air blowing 0 s and 15 s.

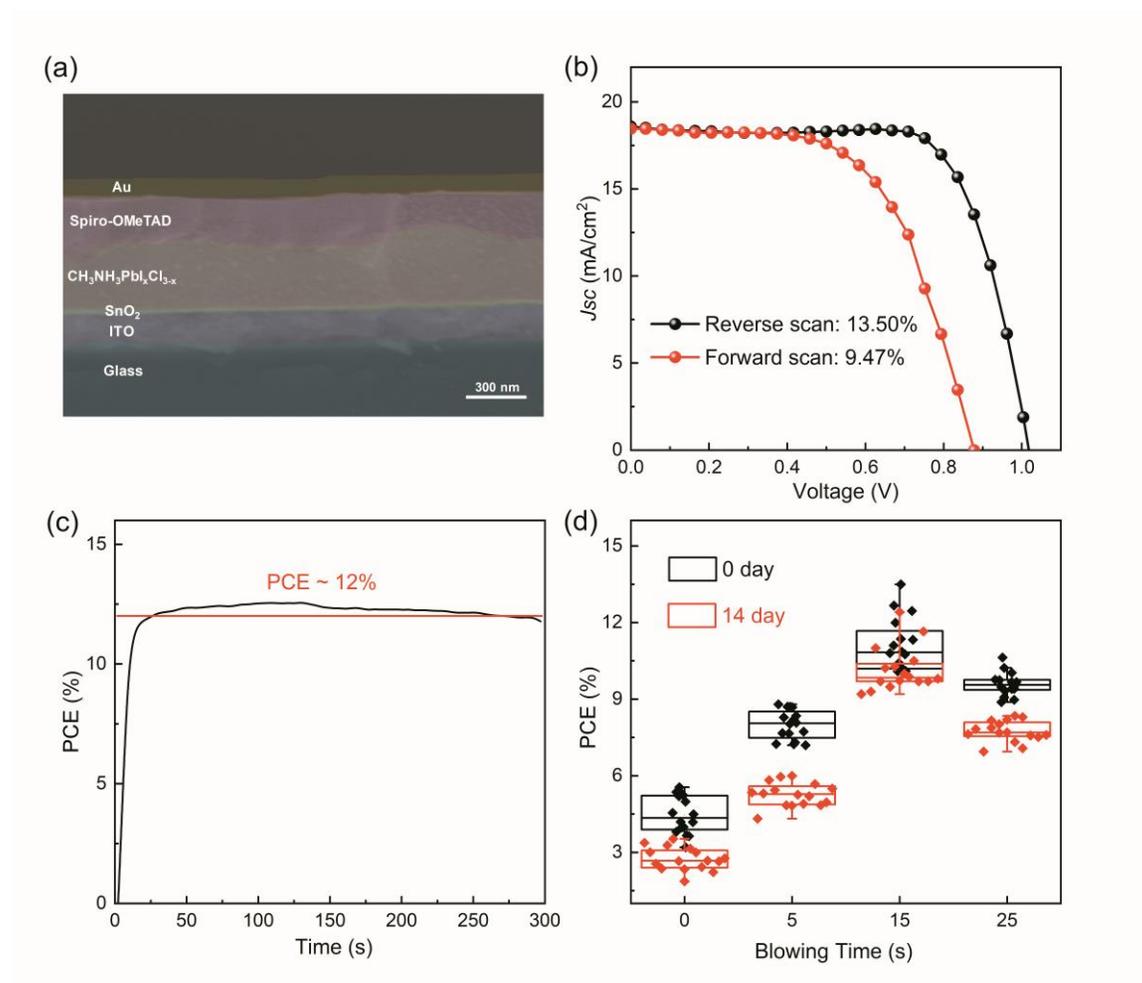
The measurement of EIS is a commonly used characterization method that indicates the carrier transport behavior in PSC devices<sup>38</sup>. The Nyquist plots of these devices were carried out under AM 1.5G with an applied bias voltage of 10 mV as shown in Figure 7a. The inside illustration of Figure 7a was the equivalent circuit. There were semicircles which were located at high frequency ranges and lines which were located at low frequency. Normally, the low frequency region represents charge recombination resistance ( $R_{rec}$ ), which the high frequency region indicates

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4 charge transport resistance ( $R_{ct}$ ). So EIS data showed the improved charge transport in PSCs with  
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6 perovskite of hot air blowing 15 s. At the same time, higher  $R_{rec}$  exposed smaller recombination  
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8 which was consistent with TRPL conclusions. On account of poor phase purity, the film blown 15  
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10 s exhibited higher  $R_{rec}$  than 30 s, which indicated that the film blown 15 s had higher recombination.  
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14 The dark current was associated with the trap density. The electron trap density was calculated  
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16 from the dark J-V curve of the electron-only device which have a structure of  
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18 ITO/SnO<sub>2</sub>/Perovskite/PCBM/Au (Figure 7b). There were Ohmic region, trap filling region and  
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20 space charge limited current region. The trap density ( $N_d$ ) was determined by the voltage at which  
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22 all the traps filled (trap-filled limit voltage  $V_{TFL}$ )<sup>39</sup>:  
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$$V_{TFL} = eN_dL^2/2\epsilon\epsilon_0 \quad (1)$$

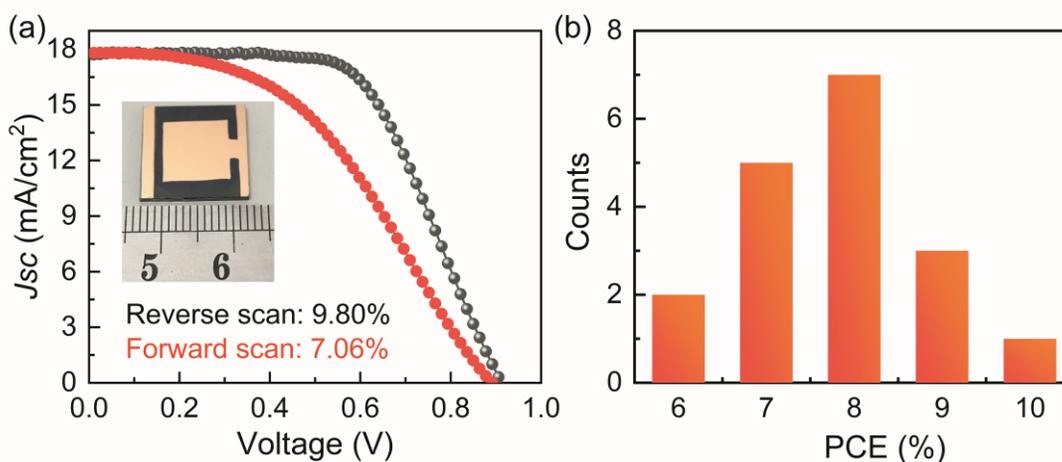
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27 where  $e$  presents elementary charge,  $L$  presents the thickness of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> film (Figure  
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29 S8),  $\epsilon$  (=32)<sup>39</sup> indicates relative dielectric constant,  $\epsilon_0$  indicates vacuum dielectric constant. The  
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31 trap density in PSCs with hot air blowing was calculated to be  $1.3 \times 10^{-16} \text{ cm}^{-3}$ , which is smaller  
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33 than the PSCs without hot air blowing ( $3.3 \times 10^{-16} \text{ cm}^{-3}$ ). The elevated trap density could be ascribed  
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35 to the higher quality of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub> films induced from hot air blowing.  
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**Figure 8.** (a) Cross-sectional SEM image of spray-coated cell. (b)  $J$ - $V$  curves with different scan direction of champion cell. (c) Stabilized power output test of champion cell. (d) Statistical results of PSC devices performance on 0 day and 14 day (stored in ambient air,  $T$ : 20~25°C,  $RH$ : 20~30%).

Figure 8a shown the cross-sectional SEM images of spray-coated cell. Figure 8b shown the different scan direction  $J$ - $V$  curves of the champion device obtained by 15 s HAB-USC (Figure S9 shown the corresponding EQE). There was severe hysteresis which could be ascribed to misaligned conduction band between  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  and  $\text{SnO}_2$ <sup>40</sup>. Compared with the spin-coated spiro-OMeTAD and  $\text{SnO}_2$ , the perovskite films prepared by spray coating have higher

roughness, resulting in poor interface<sup>33</sup>. The difference of charge transport ability between charge collection layer and perovskite layer generally attributed to more pronounced hysteresis<sup>41</sup>. Some studies have shown that adding [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) into the interface of SnO<sub>2</sub> and perovskite layer could reduce hysteresis and increase PCE<sup>42</sup>. Figure 8c shown the stabilized power output (SPO) test, which applied a constant voltage of 0.77 V for 300 s under ambient air. Figure 8d shown the statistical results of the devices efficiency decay in two weeks, which indicated the PSCs blown 15 s had better long-term stability than others especially the PSCs with substrate heating (blown 0 s). The PSCs blown 15 s still maintained an initial efficiency of over 90%.



**Figure 9.** (a) The  $J-V$  curves of 1 cm<sup>2</sup> active area PSC device with glass substrate. (b) Histogram of PCEs on account of 18 cells of 1 cm<sup>2</sup> active area with rigid substrate.

To estimate scalability of the spray coating protocols, 1 cm<sup>2</sup> devices on 16 × 16 mm glass substrate have been fabricated and achieved a champion PCE of 9.80%. The corresponding  $J-V$  curves at different scanning directions and the photograph of large-area (1 cm<sup>2</sup>) were shown in

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4 Figure 9a. The lower PCE of 1 cm<sup>2</sup> devices was ascribed to the reduced open circuit voltage ( $V_{oc}$ )  
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6 associated with relatively inhomogeneous film on large area and the reduced fill factor (FF) due  
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8 to higher series resistance. Figure 9b shown a histogram of PCEs on account of 18 cells of 1 cm<sup>2</sup>  
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10 active area with glass substrate and clearly revealed the potential of HAB-USC in the large-scale  
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12 manufacturing of PSC devices. Besides, we have prepared 1 cm<sup>2</sup> PSC devices on a flexible  
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14 substrate (ITO/PEN). Figure S10 shown the  $J-V$  curve and photograph of 1 cm<sup>2</sup> flexible device.  
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17 But the performance of flexible devices were unsatisfactory, and there were more questions we  
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19 should study deeply than that on glass substrates.  
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## 24 CONCLUSIONS

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27 We successfully deposited perovskite films using a low-cost and high volume USC technique in  
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29 ambient atmosphere. Comparing with the method of substrate heating, the method of hot air  
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31 blowing made the nucleation process during solvent evaporation more controllable. After  
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33 optimizing the spraying conditions and hot air blowing process, the sprayed PSC devices obtained  
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35 a PCE of 13.50% and maintained an initial efficiency of over 90% after two weeks. At the same  
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37 time, large-area (1 cm<sup>2</sup>) perovskite solar cells on both glass and PEN substrate was fabricated,  
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39 which shown that our spraying method combined with the novel morphology-optimization strategy  
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41 has great potential and commercial prospects in scaling up perovskite solar cells.  
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## 49 ASSOCIATED CONTENT

### 50 51 52 Supporting Information

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56 Figures S1-S10 supplied as Supporting Information.

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4 Details of optical images of  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  films prepared by single pass and multiple pass  
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6 spray routine; SEM images and XRD pattern of perovskite films prepared by SH-USC and HAB-  
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8 USC; The relationship between perovskite thickness and precursor flow rates; Measurement  
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10 method of perovskite films thickness; Cross-sectional SEM image; External quantum efficiency  
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12 spectrum of champion devices; *J-V* curve of flexible PSC device.  
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## 31 **ACKNOWLEDGMENT**

32  
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35 This work was funded by the Natural Science Foundation of Tianjin City (Grant No.  
36  
37 17JCYBJC21200, 16JCYBJC16800, 18JCQNJC71800) as well as the National Natural Science  
38  
39 Foundation of China (Grant No. 61504068). We acknowledge the Fundamental Research Funds  
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41 for the Central Universities.  
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