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# Hybrid Chemical Vapor Deposition Enables Scalable and Stable Cs-FA Mixed Cation Perovskite Solar Modules with a Designated Area of 91.8 cm<sup>2</sup> Approaching 10% Efficiency

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The development of scalable deposition methods for stable perovskite layer is a prerequisite for the development and the future commercialization of perovskite solar modules. However, scalability and stability are the two main challenges to overcome towards the realization of perovskite solar modules. In sharp contrast to previous report, here we develop a fully vapor based scalable hybrid chemical vapor deposition (HCVD) process for depositing Cs- formamidinium (FA) mixed cation perovskite films, which alleviate the problem encountered using conventional solution coating of mainly methylammonium lead iodide (MAPbI<sub>3</sub>). Using our HCVD technique, we fabricate perovskite films of Cs<sub>0.1</sub>FA<sub>0.9</sub>PbI<sub>2.9</sub>Br<sub>0.1</sub> with enhanced thermal and phase stabilities, by the intimate incorporation of Cs into FA based perovskite films. In addition, the sputtered SnO<sub>2</sub> electron transport layer (ETL) is found to be damaged during the HCVD process. In combination with precise interface engineering of SnO<sub>2</sub> ETL, we demonstrate relatively large area solar modules with efficiency approaching 10% with a designated area of 91.8 cm<sup>2</sup> fabricated on 10 cm × 10 cm substrates (14 cells in series). On the basis of our preliminary operational stability tests on encapsulated perovskite solar modules, we extrapolated that the T<sub>80</sub> lifetime is approximately 500 h (at 1 sun, 25 °C).

## 1 Introduction

The development of perovskite solar cells/modules remains unprecedented with the certified stabilized output efficiency of 20.9% for small cells (0.991 cm<sup>2</sup>), 17.25% for mini-modules (17.277 cm<sup>2</sup>) and 11.7% for submodules (703 cm<sup>2</sup>).<sup>1</sup> However, there are still two main challenges to be addressed, namely scalability and stability, towards their potential commercialization.<sup>2</sup> As learned from other photovoltaic technologies (Si, CdTe), the absolute efficiency decay with upscaling the area is estimated to be approximately 0.8%/decade.<sup>3</sup> Hence, when a 1 cm<sup>2</sup> solar cell with 20% efficiency is upscaled to a solar module of 100 cm<sup>2</sup> designated area, the efficiency is expected to be 18.4%, according to the estimated decay rate. However, at the current stage the published results in the literature indicate that for perovskite solar cell devices the efficiency decays faster upon upscaling with the area.<sup>3</sup>

This can be explained mainly by two causes. Firstly, the decay in the efficiency would be related to perovskite deposition methods. By far the most efficient perovskite solar cells are processed by the spin-coating method and reported on small active areas, e.g., 0.1 cm<sup>2</sup> to 1 cm<sup>2</sup>. A high quality perovskite film is easily obtained on this area.<sup>4</sup> However, film quality deteriorates as the film size increases to a typical module size, i.e., 100 cm<sup>2</sup>.<sup>2, 3</sup> It is thus necessary to develop perovskite deposition methods capable of depositing large area films with high quality.<sup>5</sup> Currently, scalable solution coating methods including spray coating, slot-die coating and doctor blading are in rapid development. Large area methylammonium lead iodide (MAPbI<sub>3</sub>) modules up to 45 cm × 65 cm have been demonstrated in a previous study.<sup>6</sup> However, this coating method is less efficient than that of the spin coating in small cells. Furthermore, the volatile solvents are not environmentally friendly. Beside solution coating methods, efforts have been made in utilizing vapor deposition for perovskite solar cells/modules, as it benefits from the conformal coating over large area, elimination of toxic solvents, precise film thickness control, and outstanding compatibility with tandem solar cell fabrication.<sup>7</sup> For example, the hybrid chemical vapor deposition (HCVD) process was developed to fabricate MAPbI<sub>3</sub> and formamidinium lead iodide (FAPbI<sub>3</sub>) based solar modules.<sup>8</sup> In this process, perovskite films are formed in two steps. In the first step, a lead halide film such as PbI<sub>2</sub>, PbCl<sub>2</sub> or PbBr<sub>2</sub> is deposited by thermal evaporation. In the second step, the as prepared lead halide film is reacted with

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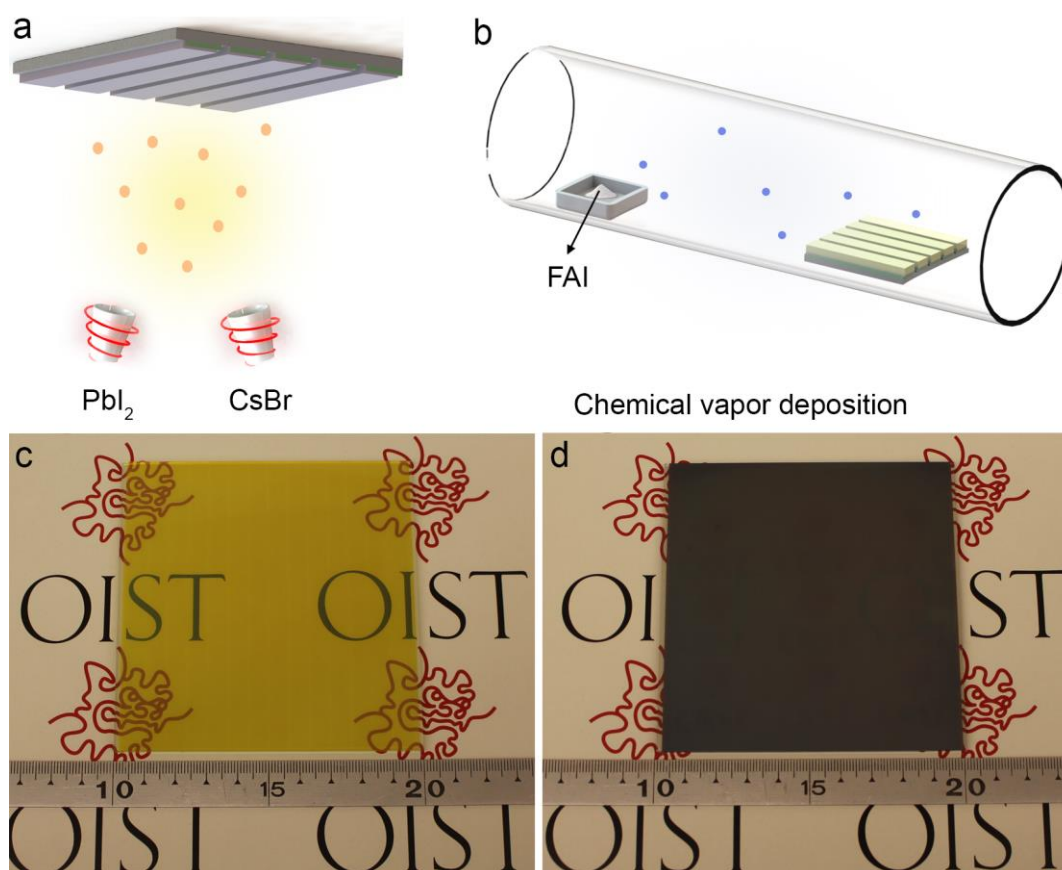
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1 organic halide species with controlled vapor atmosphere and 58 cation (especially Cs cation) perovskites to improve stability.<sup>19</sup>  
 2 pressure to form perovskite films inside a tube furnace. The 59 In FA based mixed cation perovskite, a small amount of Cs could  
 3 composition of perovskite can be readily tuned by changing the 60 stabilize the perovskite phase for high performance and  
 4 organic vapor atmosphere, from MAI to FAI or MABr, to obtain 61 stability.<sup>20</sup> In addition, with the Cs concentration in the range of  
 5 MAPbI<sub>3</sub>, FAPbI<sub>3</sub> or MAPbBr<sub>3</sub>, respectively.<sup>9</sup> With the 62 10-30%, charge-carrier mobility, charge-carrier lifetime and  
 6 controllable deposition of perovskite, HCVD is promising for 63 crystal quality are substantially improved.<sup>21</sup> A few works  
 7 large scale fabrication of high performance/stable perovskite 64 reported the solution coating of Cs containing FA based  
 8 solar cells and light emitting diodes.<sup>9</sup> Secondly, the rapid decay 65 perovskite solar cells, however, very few studies reported solar  
 9 in the efficiency can be also originated from the nonoptimal 66 modules.<sup>2, 22</sup> Our group previously reported the successful  
 10 module design (non-ohmic interconnection contact between 67 fabrication of mini-modules with Cs<sub>0.07</sub>FA<sub>0.93</sub>PbI<sub>3</sub> based  
 11 FTO/Au leading to high series resistance, large dead area due to 68 perovskite utilizing cation exchange process.<sup>23</sup> These mini-  
 12 P1, P2, P3 patterning). A likely cause responsible for the faster 69 modules showed high stability under continues light  
 13 efficiency decay upon upscaling area comes from the 70 illumination. A recent report during the preparation of this work  
 14 transparent conducting electrode sheet resistance, which often 71 is related to Cs<sub>x</sub>FA<sub>1-x</sub>PbI<sub>3-y</sub>Br<sub>y</sub> based perovskite solar modules  
 15 leads to reduction in the fill factor.<sup>10</sup> The module design of 72 fabricated using vapor-solid reaction method that could be  
 16 stripes in series connection is a solution that can significantly 73 considered as a combination of physical vapor deposition and  
 17 increase the aspect ratio of each sub-cell and reduce the 74 low pressure chemical vapor deposition.<sup>24</sup> We would like to  
 18 resistance effect. The maximum stripe width is limited by the 75 stress that these reported modules are characterized by a  
 19 transparent conducting electrode sheet resistance.<sup>11</sup> In this 76 relatively modest GFF, and relative small active areas (12 cm<sup>2</sup>  
 20 design, the relation between the stripe width and the 77 on a 5 cm × 5 cm substrate, with 6 cells in series<sup>23</sup> and 41.25 cm<sup>2</sup>  
 21 transparent conducting electrode sheet resistance should be 78 on an 8 cm × 8 cm substrate, with 9 cells in series<sup>24</sup>). To further  
 22 considered, as for each stripe there will be an area for making 79 scale up FA based mixed cation perovskites with large area and  
 23 interconnection, which is a dead area. To get lower resistance a 80 also high GFF is important for the development of perovskite  
 24 narrower stripe is required, and the active area to the total area 81 solar modules.  
 25 ratio (geometric fill factor, GFF) is also lower. In addition, using 82  
 26 mask-patterning instead of other fine controlled patterning 83 Here we show the scalability of the HCVD process in deposition  
 27 techniques such as laser scribing or mechanical scribing results 84 of FA-Cs based mixed perovskites for large area stable solar  
 28 in the GFF as low as 50%, at the early stage of the perovskite 85 modules on 10 cm × 10 cm substrates with a high GFF (90%). This  
 29 solar module design.<sup>8, 12</sup> On the basis of the calculation result, 86 fully vapor based process eliminates the use of toxic solvents  
 30 for highly conductive FTO substrates (10 Ω/□), the stripe width 87 such as dimethylformamide and dimethyl sulfoxide, which are  
 31 could be up to 7 mm with a small dead area to reach the 88 not environmentally friendly. The composition of the perovskite  
 32 maximum power output.<sup>10</sup> GFF as high as 95% has been 89 layer could be readily changed from MAPbI<sub>3</sub> to FAPbI<sub>3</sub> and FA-  
 33 demonstrated by using the laser patterning technique and this 90 Cs mixed cation perovskite, by controlling the precursor  
 34 offers a better design for active area approaching the total area 91 composition during HCVD process. With co-evaporation of CsBr  
 35 of the substrate.<sup>13</sup> 92 and PbI<sub>2</sub> in the first step, followed by exposure to FAI vapor in  
 36 93 the second step, we successfully fabricated Cs-FA perovskite  
 37 Another aspect to be considered is the operational lifetime. 94 such as Cs<sub>0.1</sub>FA<sub>0.9</sub>PbI<sub>2.9</sub>Br<sub>0.1</sub> through a fully vapor based process.  
 38 Although number of reports on the perovskite solar modules is 95 We also find that one critical issue for HCVD perovskite solar  
 39 increased gradually, they are mainly based on solution coated 96 cells/modules is the vacuum annealing process which might  
 40 MAPbI<sub>3</sub>.<sup>2</sup> With modified precursor solution properties by adding 97 damage the SnO<sub>2</sub> layer. A C<sub>60</sub> layer with a thickness of 5 nm was  
 41 surfactant, large area 57.2 cm<sup>2</sup> solar modules with doctor 98 inserted between SnO<sub>2</sub> and perovskite, which passivate and  
 42 blading MAPbI<sub>3</sub> have been fabricated with an efficiency up to 99 modulate the energy levels at these interfaces. Benefiting from  
 43 14.6%.<sup>14</sup> In another work, by adding excess MAI into the 100 the fully vapor deposition HCVD process, the film and interface  
 44 MAPbI<sub>3</sub> precursor ink, high quality film has been deposited by 101 showed little difference between small area cells and large area  
 45 blade coating and module with 12.6 cm<sup>2</sup> showed efficiency of 102 modules. With the area increasing by 1000-fold from 0.09 cm<sup>2</sup>  
 46 13.3%.<sup>15</sup> The efficiency was further improved to 15.6% with 103 to 91.8 cm<sup>2</sup>, we demonstrate that the device designated area  
 47 MA<sub>0.7</sub>FA<sub>0.3</sub>PbI<sub>3</sub> and interconnection optimization.<sup>16</sup> From an 104 PCE decreases slightly (from 13.3% to 9.34%, which corresponds  
 48 intermediate design of PbI<sub>2</sub>-nMA and MAI-mMA precursor, 105 to a PCE drop of 1.3%/decade), suggesting that this fully vacuum  
 49 solvent- and vacuum-free tape assisted coating process has 106 deposition process is a promising route towards scalability. In  
 50 been developed for MAPbI<sub>3</sub> based modules, with a certified 107 addition, the HCVD method is promising because it allows the  
 51 efficiency of 12.1% on an area of 36.1 cm<sup>2</sup>.<sup>5</sup> The slot-die coated 108 synthesis of relatively stable perovskite composition such as  
 52 perovskite solar module with an area up to 168.75 cm<sup>2</sup> was also 109 Cs<sub>0.1</sub>FA<sub>0.9</sub>PbI<sub>2.9</sub>Br<sub>0.1</sub>. The operational lifetime of these  
 53 based on MAPbI<sub>3</sub>, with the efficiency reaching 10%.<sup>17</sup> Although 110 encapsulated Glass/FTO/SnO<sub>2</sub>/C<sub>60</sub>/perovskite/spiro-MeOTAD/  
 54 the area and efficiency are increasing with research efforts, 111 Au/parylene/Glass solar modules has been studied, and showed  
 55 MAPbI<sub>3</sub> is not suitable for commercialization, due to its  
 56 instability under heat, light, humidity and oxygen.<sup>18</sup> A new trend  
 57 in the field is to employ thermally more stable FA based mixed



**Figure 1. Schematic drawing showing the HCVD process. a)** Thermal evaporation of inorganic precursors including PbI<sub>2</sub> and CsBr. **b)** HCVD of FAI organic precursor for the formation of perovskite. Optical image of **c)** co-evaporated PbI<sub>2</sub>/CsBr film and **d)** HCVD Cs<sub>0.1</sub>FA<sub>0.9</sub>PbI<sub>2.9</sub>Br<sub>0.1</sub> perovskite film (96 cm<sup>2</sup> on the 100 cm<sup>2</sup> patterned FTO substrate).

1 an extrapolated T<sub>80</sub> lifetime of approximately 500 h under one  
2 sun continuous illumination and steady state power output.

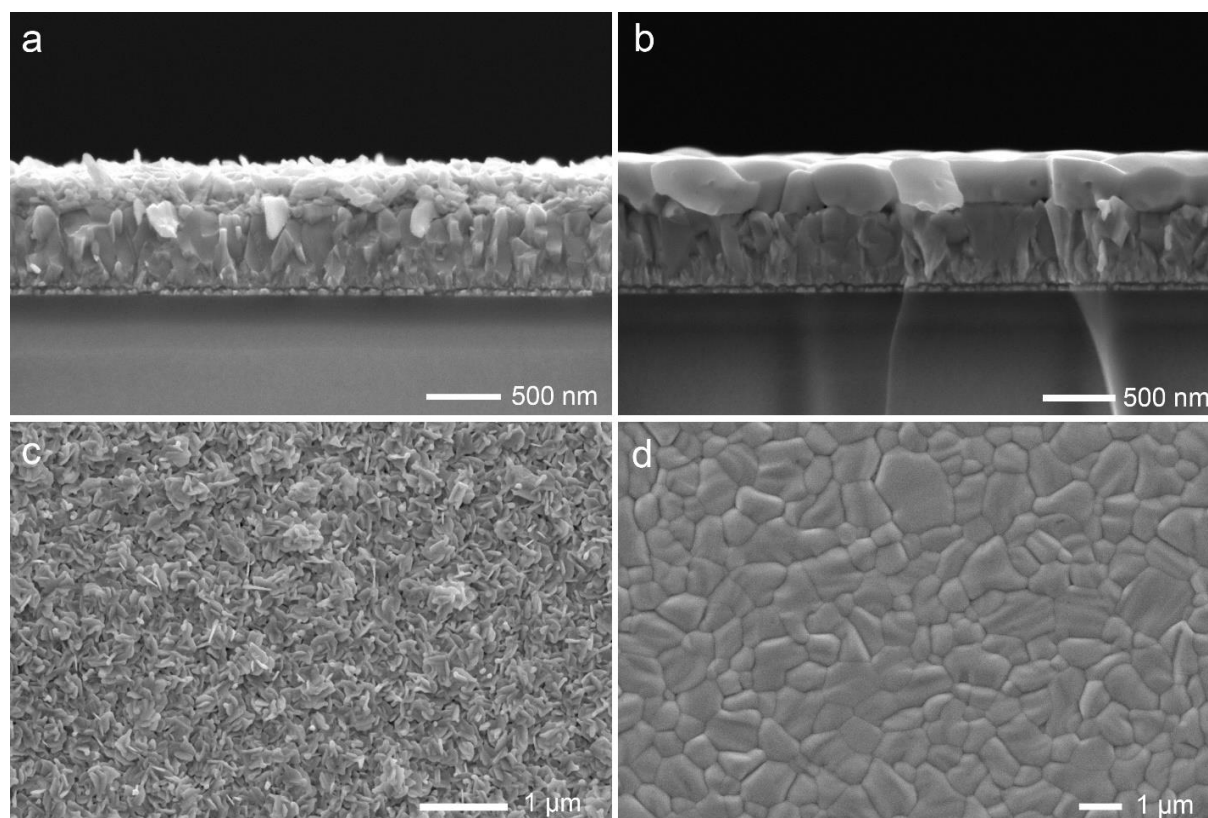
### 3 Results and discussion

#### 4 Hybrid Chemical Vapor Deposition

5 Figure 1 displays the fully vapor based HCVD process for the  
6 fabrication of perovskite films with controlled compositions.  
7 The perovskite formation proceeds into two steps as we  
8 previously developed.<sup>9</sup> The first step (Figure 1a) is slightly  
9 modified, with the vacuum co-evaporation of inorganic  
10 precursors including PbI<sub>2</sub> and CsBr. The intended composition in  
11 this work is 10% Cs and 90% FA cation, considering a suitable  
12 band-gap for single junction solar cells, phase stability, and high  
13 quality.<sup>21</sup> A small amount of Br is incorporated to further  
14 improve the perovskite stability.<sup>25</sup> Although a layer-by-layer  
15 deposition of CsBr and PbI<sub>2</sub> might help precisely control the  
16 thickness of each layer,<sup>[26]</sup> after the HCVD process, the resulted  
17 film will have a gradient composition structure because the  
18 interdiffusion of CsBr and PbI<sub>2</sub> (both are much less volatile than  
19 FAI) during the HCVD process is expected to be much slower  
20 than FAI. Based on such consideration, we employed co-  
21 evaporation on this work to ensure uniform distribution of the  
22 CsBr - PbI<sub>2</sub> mixed film. To achieve 10% Cs, the evaporation rate  
23 of PbI<sub>2</sub> and CsBr are controlled to be 0.10 nm/s and 0.01 nm/s,

24 respectively. The deposition rate and thickness of the co-  
25 evaporated film are monitored by quartz crystal microbalance  
26 (QCM). The thickness of the co-evaporated PbI<sub>2</sub>/CsBr film is  
27 approximately 185 nm. In the second step (Figure 1b), the  
28 PbI<sub>2</sub>/CsBr coated substrate is transferred into a multi-zone tube  
29 furnace with the FAI organic precursor in the upstream side and  
30 the substrates are placed in the downstream side. Upon  
31 exposure to FAI vapor and at 150 °C, PbI<sub>2</sub>/CsBr film readily  
32 converts into Cs<sub>0.1</sub>FA<sub>0.9</sub>PbI<sub>2.9</sub>Br<sub>0.1</sub> perovskite films. As shown in  
33 Figure 1c and d, the yellow co-evaporated PbI<sub>2</sub>/CsBr film and a  
34 dark brown Cs<sub>0.1</sub>FA<sub>0.9</sub>PbI<sub>2.9</sub>Br<sub>0.1</sub> perovskite film are uniformly  
35 coated on the stripe-patterned FTO substrate, with a size of 10  
36 cm × 10 cm. These results demonstrate the excellent apparent  
37 uniformity of the as-prepared Cs<sub>0.1</sub>FA<sub>0.9</sub>PbI<sub>2.9</sub>Br<sub>0.1</sub> perovskite  
38 film.

39 The microstructure of the co-evaporated PbI<sub>2</sub>/CsBr film and  
40 Cs<sub>0.1</sub>FA<sub>0.9</sub>PbI<sub>2.9</sub>Br<sub>0.1</sub> perovskite film after HCVD is further studied  
41 (Figure 2). The cross-section image of co-evaporated PbI<sub>2</sub>/CsBr  
42 film on top of FTO confirms that the PbI<sub>2</sub>/CsBr film consists of  
43 nano-plates with large roughness (Figure 2a and c). The  
44 thickness of this PbI<sub>2</sub>/CsBr layer is expected to be 185 nm,  
45 monitored by QCM during the thermal evaporation. However,  
46 due to the rough surface as shown in Figure 2a, it is difficult to  
47 determine the thickness accurately. After the HCVD process  
48 with the FAI vapor, the perovskite film thickness is  
49 approximately 400 nm (Figure 2b), and is characterized by large  
50 grains and ultra-smooth surface (Figure 2d). The film thickness



**Figure 2.** Microstructure of  $\text{PbI}_2/\text{CsBr}$  before and after HCVD. Cross-section SEM image of a)  $\text{PbI}_2/\text{CsBr}$  and b)  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  perovskite films. Surface SEM image of c)  $\text{PbI}_2/\text{CsBr}$  and d)  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  perovskite films.

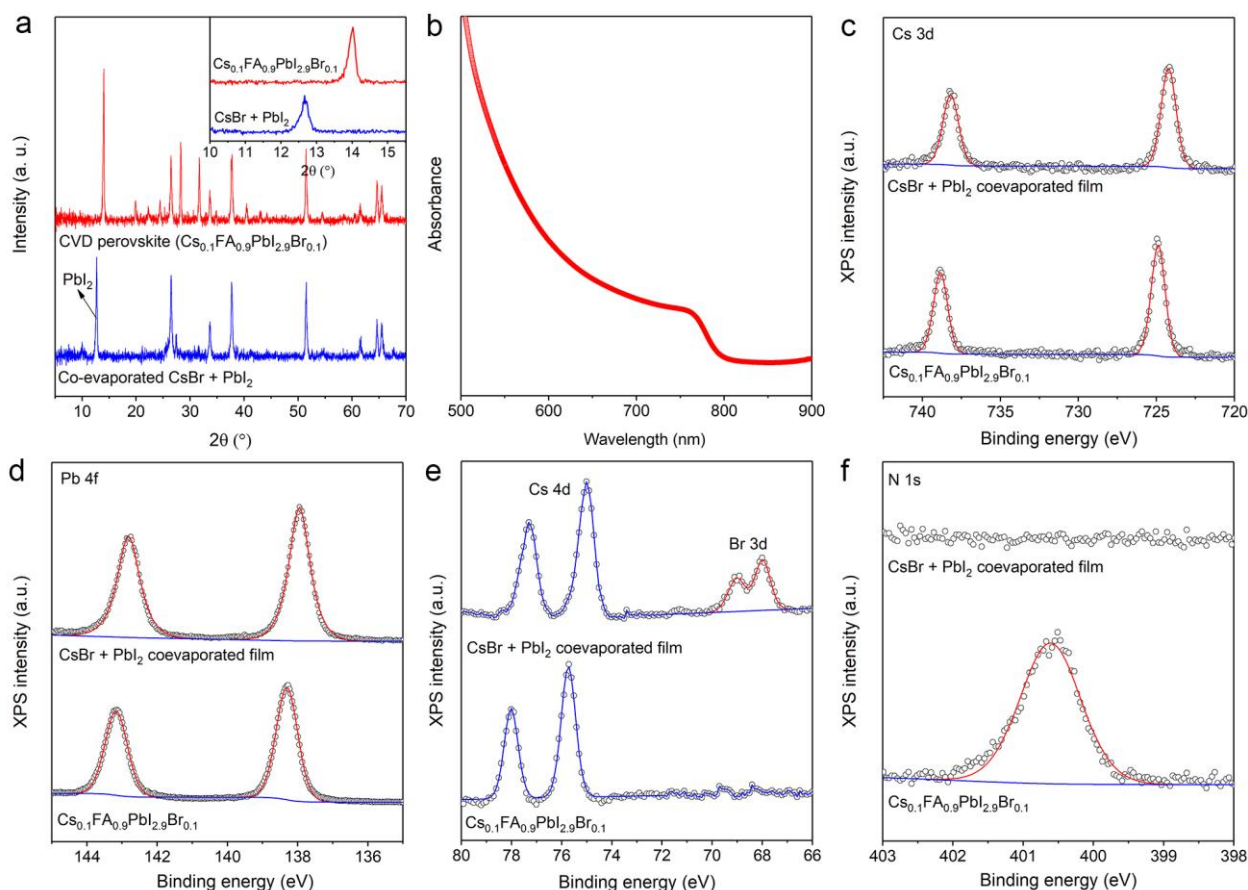
1 after the HCVD is found to increase by a factor of 2.16. The 31 confirms the uniform distribution of Cs and Br in the perovskite  
 2 thickness increase of the fully converted perovskite film could 32 layer (Figure S2). To confirm the composition,  
 3 be estimated from the density of  $\text{PbI}_2$  ( $6.16 \text{ g/cm}^3$ ) and  $\text{FAPbI}_3$  33  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  film made by solution coating process has  
 4 ( $4.10 \text{ g/cm}^3$ ).<sup>9b, 27</sup> With the assumption of full conversion and 34 been prepared and compared with  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  made by  
 5 exclusion of the small amount of Cs, the expected thickness 35 HCVD.<sup>25</sup> As shown in Figure S3-4, the XRD and UV-vis  
 6 would increase by a factor of 2.03, which is in good agreement 36 absorbance of  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  synthesized by solution and  
 7 with the cross-section SEM images (Figure 2d). These results 37 HCVD methods are very similar and thus we infer that their  
 8 confirm the excellent uniformity of the as-prepared 38 composition are also similar. The reaction of  $\text{PbI}_2/\text{CsBr}$  with FAI  
 9  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  perovskite film. 39 and annealing at  $\sim 150^\circ \text{C}$  seems to relatively decrease the  
 40 concentration of Br on the top surface of perovskite (Figure S5).

10 The crystal structure and composition of the HCVD deposited 42 indicates the incorporation of FAI for the perovskite formation  
 11  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  perovskite film have been further 43 (Figure 3f).

12 characterized. From Figure 3a the (110) perovskite peak at 44  
 13  $13.99^\circ$  is clearly observed without any residual  $\text{PbI}_2$  signal at  
 14  $12.6^\circ$  after HCVD (inset in Figure 3a), which confirms that FAI  
 15 could diffuse into the bottom and completely react with  
 16  $\text{PbI}_2/\text{CsBr}$  film. Furthermore, no diffraction peaks appear at  
 17  $11.7^\circ$  corresponding to the non-perovskite phase of  $\text{FAPbI}_3$ ,  
 18 suggesting the good phase purity of the  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$ ,  
 19 perovskite films prepared by HCVD. The optical absorbance 45  
 20 edge of the perovskite film is 798 nm (Figure 3b), which 46  
 21 corresponds to an optical band of 1.56 eV from Tauc-plot 47  
 22 (Figure S1). To study the composition of the perovskite film, X- 48  
 23 ray photoelectron spectroscopy (XPS) is performed (Table S1). 49  
 24 Before and after HCVD the ratio between Cs and Pb is 50  
 25 approximately 0.1, which is consistent with deposition rate 51  
 26 monitored by QCM (Figure 3c and d). After HCVD, the core level 52  
 27 of Br 3d is weaker (Figure 3e).<sup>[28]</sup> Regarding the decreased Br 3d 53  
 28 signal, whether this is because there is phase separation on the 54  
 29 top surface or the Br actually evaporates after HCVD process is 55  
 30 currently under further investigation. The XPS mapping further 56  
 57  
 58

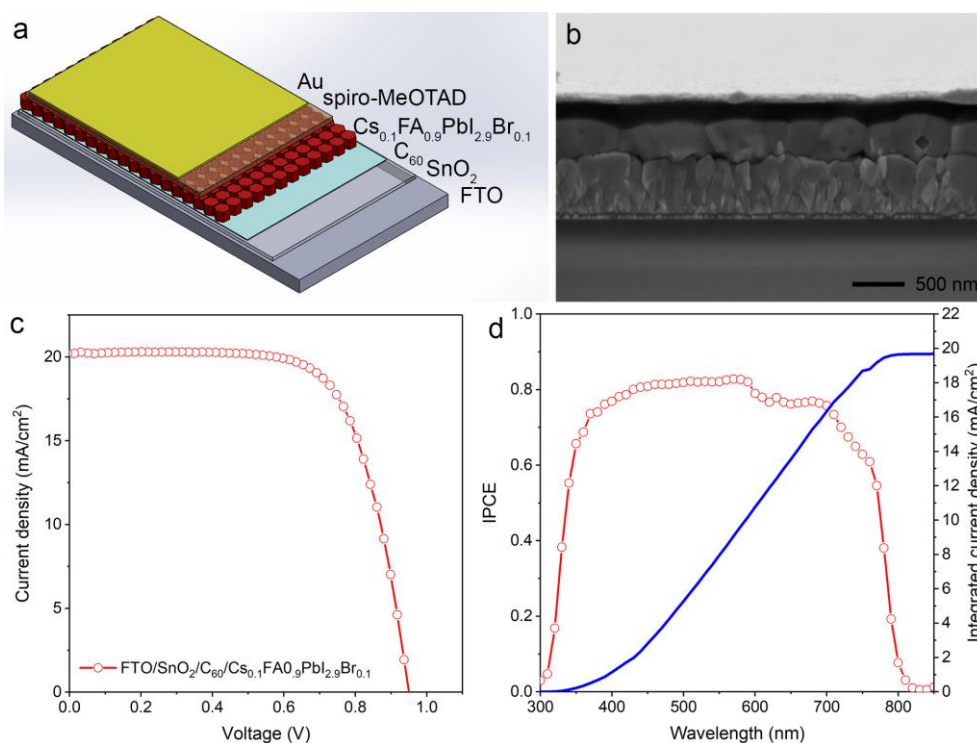
#### 44 Small area solar cells

45 The carrier lifetime of  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  on bare glass made by  
 46 HCVD was investigated by time-resolved photoluminescence  
 47 (TRPL), as presented in Figure S6. The upper limit of the open-  
 48 circuit voltage ( $V_{oc}$ ) due to the non-radiative recombination in  
 49 the perovskite is calculated to be approximately 1.04 V at room  
 50 temperature (Supporting Note 1).<sup>11, 29</sup> Further study are  
 51 necessary to improve the film quality and to reduce the defects  
 52 density to achieve long carrier lifetime.<sup>30</sup> To check the  
 53 photovoltaic performance of this HCVD deposited  
 54  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  film, a planar junction structured device has  
 55 been applied with sputtered  $\text{SnO}_2$  as electron transport layer  
 56 (ETL) (Figure 4a). The sputtered  $\text{SnO}_2$  film has been optimized  
 57 according to our recent work and achieves an efficiency over  
 58 20% based on spin coated perovskite films.<sup>31</sup> However, the

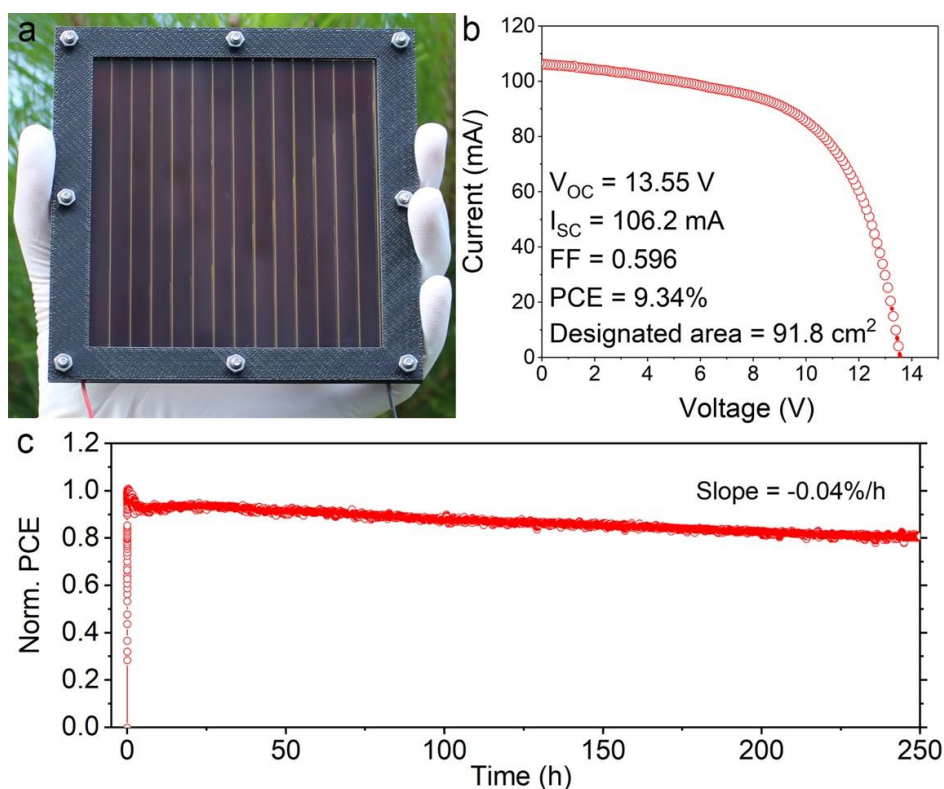


**Figure 3. Structure and composition of HCVD perovskite layer.** a) XRD before and after HCVD, which indicate high quality perovskite structure. b) Optical absorbance of  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$ . Core level of c) Cs 3d, d) Pb 4f, e) Br 3d and f) N 1s before and after HCVD, which indicate the formation of  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$ .

1 HCVD device performance is lower than expected. As shown in 30 glove box) where oxygen defect deteriorate the perovskite solar  
 2 Figure S7, from the typical J-V curves of the solar cells, the  $V_{\text{OC}}$  31 cells performance.<sup>34</sup>  
 3 is average only 0.81 V (Table S2), which is much lower than the  
 4 calculated upper limit due to the non-radiative recombination  
 5 (1.04 V). We find that the vacuum annealing process during 32 In this case,  $\text{SnO}_2$  surface modification is necessary to achieve  
 6 HCVD damages the  $\text{SnO}_2$  layer. Ultraviolet photoemission 33 high quality for electron extraction and hole blocking. A thin  
 7 spectroscopy (UPS) and XPS measurements of the  $\text{SnO}_2$  layer 34 layer of  $\text{C}_{60}$  has been evaporated on top of  $\text{SnO}_2$  before co-  
 8 before and after vacuum annealing process have been 35 evaporation of  $\text{PbI}_2/\text{CsBr}$  as a buffer and passivation layer. The  
 9 performed to study the gap states (Figure S8). These states are 36 energy level diagram from UPS measurement is shown in Figure  
 10 believed to be mainly caused by oxygen deficiency after vacuum 37 S11, which confirms the smooth transfer of charges crossing the  
 11 annealing (Figure S9). These gap states after the vacuum 38 interface.<sup>35</sup> Regarding the influence on the  $\text{SnO}_2$  films induced  
 12 annealing process lower the hole-blocking properties of the 39 by vacuum annealing, we further performed a control  
 13  $\text{SnO}_2$  ETL.<sup>31, 32</sup> To confirm the effect of the vacuum annealing 40 experiment on a sputtered  $\text{SnO}_2/\text{C}_{60}$  electron transport layer  
 14 process, a control experiment has been performed. Solution 41 before and after vacuum annealing to study the effect of  $\text{C}_{60}$   
 15 processed devices were fabricated on sputtered  $\text{SnO}_2$  with and 42 passivation (Table S3). Note that in the case of “ $\text{SnO}_2/\text{C}_{60}$ ”, the  
 16 without vacuum annealing process. As shown in Table S3 and 43 efficiency with vacuum annealing is only slightly lower than that  
 17 Figure S10, the photovoltaic performance of solution coated 44 without vacuum annealing, suggesting that the negative effect  
 18 perovskite solar cells on sputtered  $\text{SnO}_2$  with and without 45 of vacuum annealing is largely mitigated by adding a thin film of  
 19 vacuum annealing process differ significantly. After vacuum 46  $\text{C}_{60}$  with a thickness of 5 nm. However, when comparing the  
 20 annealing the  $\text{SnO}_2$  performance degrades significantly, and all 47 case of  $\text{SnO}_2/\text{C}_{60}$  with the case of  $\text{SnO}_2$  before vacuum  
 21 the device photovoltaic parameters decrease. Especially the  $V_{\text{OC}}$  48 annealing, the device efficiency is about 10-20% lower in the  
 22 decreases from 1.03 V to 0.73 V. As a control experiment the 49 case of  $\text{SnO}_2/\text{C}_{60}$ . The factor that might influence the device  
 23 vacuum annealing effect has also been studied based on mostly 50 performance in the case of  $\text{SnO}_2/\text{C}_{60}$  is air exposure during the  
 24 used  $\text{SnO}_2$  film prepared from Alfa Aesar solution.<sup>[33]</sup> This 51 sample transfer. It has been shown that  $\text{C}_{60}$  has poor air  
 25 crystalline  $\text{SnO}_2$  film also shows reduced performance after 52 stability, which may induce oxygen-trap states and decrease  
 26 vacuum annealing process (Table S3). It shows that the negative 53 charge carrier lifetime.<sup>[36]</sup> Air exposure after  $\text{C}_{60}$  deposition is  
 27 effect induced by vacuum annealing is not limited to sputtered 54 proposed to be the main reason for the lower performance.  
 28  $\text{SnO}_2$  films. Note that this is not unique to  $\text{SnO}_2$ , because it also 55 With this vacuum deposited  $\text{SnO}_2/\text{C}_{60}$  bilayer as ETL, solar cells  
 29 occurs for  $\text{TiO}_2$  annealed in inert atmosphere (such as in  $\text{N}_2$  56 based on perovskite  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  made by HCVD have



**Figure 4.**  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  based planar junction solar cell performance. a) Schematic drawing showing the planar junction device structure. b) Cross-section SEM image of the HCVD  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  based solar cell. Typical c) J-V curve and d) IPCE spectra of HCVD  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  based solar cells.



**Figure 5.**  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  based solar module performance. a) Optical image of a 10 cm  $\times$  10 cm HCVD  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  based solar module. b) J-V curve of the champion 10 cm  $\times$  10 cm HCVD  $\text{Cs}_{0.1}\text{FA}_{0.9}\text{PbI}_{2.9}\text{Br}_{0.1}$  based solar module (14 sub-cells in series). c) Operational stability of HCVD solar module under one-sun illumination and steady-state power output tracking.

1 been fabricated with the structure 4 be observed in the cross-section SEM image (Figure 4b). The 2 Glass/FTO/SnO<sub>2</sub>/C<sub>60</sub>/Perovskite/spiro-MeOTAD/Au (Figure 4a). 5 active layer thickness is around 400 nm. With this planar 3 A clear layer by layer structure of the planar junction device can 6 junction structure the champion small cell efficiency is 13.3%

1 (0.09 cm<sup>2</sup>). Improving the perovskite optoelectronic quality and 58 PCE<sub>Forward</sub>)/PCE<sub>Reverse</sub>) (Figure S16),<sup>39</sup> which need further  
 2 engineering the perovskite and ETL interfaces to reducing the 59 engineering of interface and perovskite composition.<sup>33, 39</sup> As a  
 3 non-radiative carrier recombination rates at bulk and interfaces 60 demonstration of the broad composition adjustment of  
 4 are possible strategies to further push up the solar cell 61 perovskite by HCVD, the same 10 cm × 10 cm size modules but  
 5 performance. As shown in Figure 4c, from the typical J-V curve 62 with MAPbI<sub>3</sub> active layer have been fabricated. The  
 6 of solar cells with HCVD Cs<sub>0.1</sub>FA<sub>0.9</sub>PbI<sub>2.9</sub>Br<sub>0.1</sub>, the V<sub>OC</sub> is on 63 performance is lower than that of the Cs<sub>0.1</sub>FA<sub>0.9</sub>PbI<sub>2.9</sub>Br<sub>0.1</sub> based  
 7 average 0.90 V (Table S2). The short circuit current density (J<sub>SC</sub>) 64 solar modules (Figure S17), due to the mismatch of the energy  
 8 is around 20.2 mA/cm<sup>2</sup>, which is consistent with IPCE spectra 65 level alignment as shown in Figure S11. This demonstrates the  
 9 (Figure 4d). Currently, the average fill factor is around 0.67 66 scalability of our HCVD method for large area monolithic  
 10 leaving room for further improvement. 67 perovskite solar modules, with desired composition.

## 11 Large area solar modules

12 The deposition process is very promising for large scale solar  
 13 module fabrication. The scale-up of the Cs<sub>0.1</sub>FA<sub>0.9</sub>PbI<sub>2.9</sub>Br<sub>0.1</sub> solar  
 14 cells to 10 cm × 10 cm solar modules through the HCVD method  
 15 is further demonstrated (Figure 5a). The module comprises 14  
 16 sub-cells in series connection. For each FTO stripe, the width is  
 17 6.6 mm, with 0.1 mm P1 patterning in between each FTO stripe.  
 18 The length of the stripe is 98 mm results in the area of 6.468  
 19 cm<sup>2</sup> for each stripe. The interconnection area is formed by CO<sub>2</sub>  
 20 laser scribing, with a width around 0.15 mm (P2). Finally,  
 21 mechanical scribing is used to separate each sub-cell by forming  
 22 a P3 patterning (0.05 mm). The P1-P2-P3 patterning is shown in  
 23 Figure S12. Considering the FTO stripe width plus P1 width (6.7  
 24 mm) and the dead area for sub-cell series connection (0.68  
 25 mm), the geometric fill factor is up to 90%. 10 solar modules  
 26 have been fabricated, the photovoltaic parameters of which are  
 27 listed in Table S4. The champion solar module is plotted in  
 28 Figure 5b. The modules have been further encapsulated by  
 29 deposition of a Parylene film<sup>37</sup> on top of Au electrode side and  
 30 then a cover glass is sealed on top with UV-curable glue on the  
 31 edges to further prevent water and oxygen infiltration as well  
 32 as to ensure a good thermal contact with cooling stage to  
 33 dissipate heat (Figure S13). This low temperature encapsulation  
 34 process does not affect the module performance (Figure S14).  
 35 The best performance is 9.34% with a designated area of 91.8  
 36 cm<sup>2</sup> (Figure 5b) and the active area efficiency reaches 10.37%  
 37 (active area = 82.6 cm<sup>2</sup>).

38 With a GFF of 90%, the short-circuit current (I<sub>SC</sub>) is expected to  
 39 be 119 mA considering the J<sub>SC</sub> value obtained from the small cell  
 40 (20.2 mA/cm<sup>2</sup>) and the area of each cell stripe (5.909 cm<sup>2</sup>).  
 41 Indeed, the measured I<sub>SC</sub> from solar modules is mostly around  
 42 110 mA (Table S4), which clearly demonstrates the fine  
 43 patterning process and the scalability of our HCVD method. The  
 44 average V<sub>OC</sub> for modules is 12.8 V and for each sub-cell is 0.91  
 45 V. The V<sub>OC</sub> of sub-cells in the modules also matches well the  
 46 value obtained for the small area cells (Table S2 and S4). From  
 47 the small area cells to modules, the area is enlarged by over  
 48 1000 time (from 0.09 cm<sup>2</sup> to 91.8 cm<sup>2</sup>). The champion efficiency  
 49 decreased from 13.3% to 9.3% (active area efficiency 10.4%)  
 50 (Figure S15), which is only slightly lower than expectation  
 51 (10.9%) if assuming an efficiency-against-area decay rate of  
 52 0.8%/decade. The decrease mainly comes from the lower fill  
 53 factor. Without removing bottom SnO<sub>2</sub> (17 nm), the contact  
 54 resistance might also increase compared with Au/FTO interface  
 55 contact resistance, which might be the main cause for the lower  
 56 fill factor.<sup>38</sup> This module shows hysteresis with a hysteresis  
 57 factor around 0.17 (hysteresis factor = (PCE<sub>Reverse</sub> -

68 The HCVD method for mixed cation perovskite is promising for  
 69 stable solar modules. Here the operational lifetime is measured  
 70 with encapsulated 5 cm × 5 cm mini-modules with designated  
 71 area of 22.4 cm<sup>2</sup>. The module consists of 7 cells connected in  
 72 series and exhibit designated area efficiency around 10%, which  
 73 is consistent with a decay rate of 1.3%/decade (Figure S15 and  
 74 18). The operational lifetime was measured under a controlled  
 75 temperature of 25 °C and continuous one-sun illumination with  
 76 steady state power output. From Figure 5c we can first observe  
 77 a burn-in loss of power output within approximately the first ten  
 78 hours with 90% of its initial performance remaining.<sup>40</sup> A slow  
 79 decay of the performance with a slope of -0.04%/h follows the  
 80 burn-in loss, which corresponds to a T<sub>80</sub> lifetime of 500 h.<sup>41</sup>  
 81 These results demonstrate the good long-term stability of the  
 82 Cs<sub>0.1</sub>FA<sub>0.9</sub>PbI<sub>2.9</sub>Br<sub>0.1</sub> based solar module through our HCVD  
 83 method.

## 84 Conclusions

85 In summary, with the mix-cation Cs/FA based perovskite films  
 86 deposited by HCVD, the SnO<sub>2</sub>/C<sub>60</sub> ETL deposited by sputtering  
 87 and thermal evaporation, and the Parylene encapsulation layer  
 88 deposited by chemical vapor deposition, fully scalable  
 89 perovskite solar modules with 91.8 cm<sup>2</sup> designated area on 100  
 90 cm<sup>2</sup> substrates are developed. Based on the fully vapor  
 91 deposition process there is no limitation for the module area  
 92 and the absolute efficiency decay is consistent with other  
 93 commercialized photovoltaic techniques when scaling-up. The  
 94 operational T<sub>80</sub> lifetime under illumination is extrapolated  
 95 approximately 500 h. With further interface engineering and  
 96 perovskite film post treatment, the device performance is  
 97 promising for improvement. We believe that HCVD will be a  
 98 strong tool for perovskite photovoltaic towards  
 99 commercialization.

## 101 Experimental

102 **HCVD:** The HCVD process is performed in a multi-zone tube  
 103 furnace with solid FAI power as the precursor. The FAI power is  
 104 first converted to the gas phase in the upstream zone when  
 105 heated up to 190 °C. With the assistance of a low flux of carrier  
 106 gas (air with a relative humidity of 45% in this case; flux = 60  
 107 sccm), the gas phase FAI is driven uniformly towards the  
 108 downstream zone where the chemical reaction takes place  
 109 between FAI and the pre-deposited CsBr/PbI<sub>2</sub> substrate. The



1 other end of tube furnace is connected to a pump, which results 57 of 2 mm. This Parylene film was reported to be resistant to  
 2 in an overall average vacuum level of approximately 1 torr in the 58 water.<sup>37</sup>  
 3 furnace. The temperature of the downstream zone is 59  
 4 approximately 150 °C. The pressure at the end with the input 60 *Characterization*: The absorbance spectra of perovskite were  
 5 carrier gas is expected to be slightly higher and gradually 61 recorded with a UV-vis spectrometer (Jasco V-670). The  
 6 decrease towards the end connected to the pump. The gentle 62 ultraviolet photoemission spectroscopy (UPS) and X-ray  
 7 gradient of pressure along the tube serves as the driving force 63 photoelectron spectroscopy (XPS) spectra were recorded from  
 8 to move FAI vapor from one end to the other. During HCVD, the 64 XPS-AXIS Ultra HAS (Kratos) equipped with monochromatic Al-  
 9 FAI powder source is abundant, therefore to the first order 65  $K\alpha=1486.6$  eV and non-monochromatic He-I= $21.22$  eV sources.  
 10 approximation we can consider the FAI concentration in the gas 66 Sample damage induced by UV and X-ray was monitored by  
 11 stream to be a constant along the tube, if we do not take into 67 taking five consecutive scans. Surface morphology and cross-  
 12 account the slight decrease of the FAI concentration down the 68 section characterization were performed using a scanning  
 13 stream due to a small amount of FAI reacting with the CsBr/PbI<sub>2</sub> 69 electron microscope (FEI Quanta 250 FEG). Crystal structure of  
 14 substrates. According to the equation  $D_g \propto T^{3/2}/P$  (where  $D_g$  is 70 perovskite was measured by an X-ray Diffractometer (XRD)  
 15 the diffusion constant, T is the temperature, and P is the 71 (Bruker D8 Discover). Time resolved photoluminescence (TRPL)  
 16 pressure),<sup>[9b]</sup> the diffusion rate of gas phase FAI to the substrate 72 of perovskite film on bare glass was acquired using the time-  
 17 is approximately a constant. Also, the adsorption rate of FAI on 73 correlated, single-photon counting technique (Hamamatsu,  
 18 the substrate can be assumed to be a constant independent (or 74 C10627), and excitation was provided by a femtosecond mode-  
 19 only has a weak dependence) of the deposited film thickness. 75 locked Ti:sapphire laser (SpectraPhysics, MAITAI XF-IMW) at  
 20 As a result, the film thickness of the deposited FAI is determined 76 450 nm. J-V curves of solar cells/modules were recorded by a  
 21 by the total deposition time and will be uniform across the 77 Keithley 2420 Source Meter. The simulated AM1.5 solar light  
 22 entire length of the tube furnace. 78 comes from a solar simulator (Oriel-Sol1A equipped with a 450

23 79 W Xe lamp and an AM1.5 filter), with an illumination intensity  
 24 *Solar cell/module fabrication*: Patterned FTO glass with sheet 80 of 100 mW/cm<sup>2</sup> calibrated by a reference Si solar cell. The  
 25 resistance around 7  $\Omega/\square$  (OPVT) was first ultrasonic washed 81 designated area of 0.09 cm<sup>2</sup> for small cells, 22.4 cm<sup>2</sup> for small  
 26 sequentially with 1 wt% sodium dodecyl sulfate aqueous, de- 82 modules and 91.8 cm<sup>2</sup> for large modules were defined by  
 27 ionized water, acetone and isopropanol for 15 min. The dry FTO 83 corresponding metal mask. For solar cells/modules  
 28 substrate was then sputtered coated with 17 nm SnO<sub>2</sub> and 84 characterization, the dwell time is 10 ms, with small cell in the  
 29 evaporated with 5 nm C<sub>60</sub>, with deposition rate of 0.7 nm/min 85 range of -0.1 V to 1.2 V, 5 cm × 5 cm modules in the range of -  
 30 and 0.02 nm/s, respectively. The perovskite active layer was 86 0.1 V to 7.0 V and 10 cm × 10 cm modules in the range of -1 V  
 31 deposited by HCVD developed in our early work,<sup>8-9</sup> with 87 to 14.0 V. The EQE spectra of small cells were characterized by  
 32 different precursor composition. PbI<sub>2</sub> and CsBr were thermally 88 Oriel IQE 200.

33 co-evaporated on C<sub>60</sub> coated FTO/SnO<sub>2</sub> substrate with a rate of  
 34 0.10 nm/s and 0.01 nm/s, respectively, for 185 nm. The  
 35 PbI<sub>2</sub>/CsBr coated substrate was then transferred to a multi-zone 89 **Conflicts of interest**  
 36 tube furnace. The Cs salt is sensitive to water. To avoid the 90 There are no conflicts to declare.  
 37 moisture effect, the tube furnace was quickly pumped down to  
 38 1 torr after loading the CsBr/PbI<sub>2</sub> substrate. The FAI vapor was  
 39 carried by air with a humidity of 45%. The mixed O<sub>2</sub>/N<sub>2</sub> carrier 91 **Acknowledgements**  
 40 gas helps passivate shallow and deep traps in the converted 92 This work was supported by funding from the Energy Materials  
 41 perovskite film.<sup>[42]</sup> On the other hand, with such a low pressure 93 and Surface Sciences Unit of the Okinawa Institute of Science  
 42 level of air (1 torr) and the substrate temperature at 94 and Technology Graduate University, the OIST Proof of Concept  
 43 approximately 150 °C, we expect the moisture in the carrier gas 95 (POC) Program, the OIST R&D Cluster Research Program, and  
 44 to have a minimal negative impact on the final perovskite 96 JSPS KAKENHI Grant Number JP18K05266. We would like to  
 45 film.<sup>[43]</sup> After reaction and cooling the perovskite film was 97 thank OIST Mech. Eng. & Microfabrication Support Section for  
 46 washed with saturated potassium iodide solution (isopropanol) 98 maintenance of cleanroom and sputtering equipment.

47 and annealed under 100 °C for 20 min. A hole transport material  
 48 solution containing 29 mg spiro-MeOTAD, 11.5  $\mu$ L TBP, and 7  $\mu$ L  
 49 Li-TFSI solution (520 mg/mL in acetonitrile) in 0.4 mL 99 **Notes and references**  
 50 chlorobenzene was spin coated on top of the perovskite layer.  
 51 For solar module the P2 patterning was performed by a CO<sub>2</sub> 100 1  
 52 laser with a power of 5.6 W. At the end, 120 nm Au was 101  
 53 thermally evaporated as back contact electrode and separated 102  
 54 each sub-cell by mechanical scribing to form P3 patterning. The 103 2  
 55 solar modules were encapsulated by 2  $\mu$ m thick chemical vapor 104 3  
 56 deposited Parylene and sealed by a cover glass with a thickness 105 4  
 106 5  
 107 6  
 108 7

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