

1 **Modulating crystal growth of formamidinium-cesium perovskites for**
2 **over 200-cm² photovoltaic sub-modules**

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20 **Abstract**

21 Upscalable fabrication of efficient and stable perovskite solar modules is urgently needed for
22 commercialization. Herein, we introduce methylammonium chloride (MACl) additives in the co-
23 solvent system of N-methyl-2-pyrrolidone (NMP) / N,N-dimethylformamide (DMF) to control the
24 formation of intermediate phases during the growth of formamidinium (FA)-cesium (Cs) lead
25 triiodide perovskite films. We achieve high quality films upon drying without the use of antisolvent.
26 By implementing bulk and surface passivation, the champion efficiencies of 24.02% for a small-
27 sized solar cell and 20.5% for a 5 cm × 5 cm solar mini-module on an aperture area of 22.4 cm²
28 (geometrical fill factor is ~96%) are achieved by spin-coating. The fully blade-coated perovskite

29 solar sub-module demonstrates a champion efficiency of 15.3% on an aperture area of 205 cm². The
30 solar mini-module exhibits impressive operational stability with a T80 lifetime over 1000 hours at
31 maximum power point tracking (MPPT) under continuous light illumination.

32 **Introduction**

33 Owing to the outstanding optoelectronic properties of hybrid organic-inorganic metal halide
34 perovskite materials such as high absorption coefficient, long carrier diffusion length, and low trap
35 density, over 25% power conversion efficiencies (PCEs) have been achieved for small-sized
36 perovskite solar cells (PSCs)¹⁻³. However, the realization of large-scale, high-efficiency and stable
37 perovskite solar modules (PSMs) still faces a number of technological hurdles for the widespread
38 commercial application at present⁴⁻⁷. It has been proposed that the major issues are due to a lack of
39 control when upscaling the manufacturing process, such as the homogeneity of perovskite
40 composition and morphology which affect the reproducibility and long-term stability of the PSMs^{7,8}.

41 Recently, an increasing number of research works have been devoted to improving both the PCE
42 and stability of perovskite solar mini-modules from the viewpoints of scalable deposition
43 engineering^{4,9}, perovskite compositions¹⁰⁻¹², electron/hole transport materials as well as the
44 corresponding interfaces¹³⁻¹⁷. Undoubtedly, the scalable fabrication of a large-area high-quality
45 perovskite light absorber layer remains elusive. To achieve highly efficient and stable PSMs, typical
46 three-dimensional (3D) formamidinium (FA, NH₂CH=NH₂⁺)-based lead triiodide perovskite has
47 become the widely studied composition due to its narrower bandgap (*E_g*) and better thermal stability
48 compared to the methylammonium (MA, CH₃NH₃⁺)-based counterparts¹⁸⁻²⁰. A lot of strategies, such
49 as solid-reaction by chemical vapor deposition²¹, one-step and two-step solution processes such as
50 slot-die coating, inkjet printing, and spray coating²²⁻²⁶, have also been employed to upscale large-
51 area high-quality FA-based perovskite films. Among them, one-step solution printing techniques
52 such as blade coating and slot-die coating are promising methods with low cost and convenience in
53 scalable fabrication²⁷, which also demonstrated impressive efficiencies for perovskite solar mini-
54 modules by combining with proper additive engineering^{9,10,23}. For example, Huang and coworkers
55 reported a blade coated FA-based perovskite solar mini-module with PCE over 19% on an aperture
56 area of 50 cm² by introducing a solid-state lead coordinating additive of carbonylhydrazide (CBH) to
57 modify the interfacial properties between the perovskite and substrate²⁸. Seok and coworkers also
58 reported a bar coated FA-based perovskite solar mini-module with an efficiency of 20.4% on an

59 aperture area of 31 cm² via additive engineering of n-cyclohexyl-2-pyrrolidone (CHP) for
60 improving the morphology of the perovskite layer²⁹. However, the investigation on printing
61 perovskite solar sub-modules with an area larger than 200 cm² is still lacking. How to upscale high-
62 quality large-scale perovskite films and assemble them into sub-modules with a minimum PCE
63 penalty are still challenging at present, which is also an essential step towards panel-scale solar cells.

64 If the compact perovskite film can be formed just from the self-drying condition (Self-drying
65 herein means that the solvent of the perovskite precursor ink volatilizes naturally at room
66 temperature without assistance of any other process such as heating, spinning, blowing, *etc*), the
67 upscaling printing process will be easier and more efficient (i.e., more convenient, lower cost, and
68 higher reproducibility). Based on this rationale, it is essential to develop a suitable perovskite
69 precursor ink for growing high-quality perovskite films for large-scale sub-modules. In our previous
70 study, we provided a lead halide-templated crystallization process for printing large-area FA-based
71 perovskite films, to minimize the formation of undesirable perovskite-DMF complex intermediates
72 that could induce dendritic crystals^{24,30}. The competition between the lead halide-NMP adducts and
73 the perovskite-DMF complex intermediates dominates the morphology and crystallinity of the final
74 FA-based perovskite films. The presence of an ample amount of CsI (17%) and lead chloride (PbCl₂)
75 helps to improve the morphology, suppress the δ -phase formation and stabilize the final α -phase
76 perovskite film³¹⁻³³, however, it enlarges the bandgap and thus lowers the efficiency of eventual
77 solar modules. The introduction of a proper amount of MAcl additives is another widely used
78 strategy for improving the morphology and stabilizing the α -phase of FA-based perovskite within
79 the one-step or two-step methods³⁴⁻³⁶. However, the effect of MAcl additives on nucleation and
80 growth of self-drying perovskite films is not fully understood, which is essential information to
81 overcome the challenges in improving the quality of large-area films.

82 In this work, we report a modulation strategy of self-drying FA-Cs perovskite precursor ink for
83 scalable fabrication of large-scale perovskite solar sub-modules. **Fig. 1a** presents the configuration
84 of the perovskite solar sub-module with the scalable deposition strategy of each functional layer. A
85 proper amount of MAcl additives is introduced into a narrower bandgap (~1.55 eV) FA_{0.88}Cs_{0.12}PbI₃
86 perovskite-NMP/DMF precursor ink to realize the scalable printing of high-quality perovskite layers.
87 In our initial exploration, we found that the lower formation energy of FA-Cs-alloyed perovskites
88 would contribute to the growth of high-quality α -phase films (**Supplementary Fig. 1 and**

89 **Supplementary Note 1**). Due to the lower formation energy through the incorporation of MACl in
90 the FAPbI₃ perovskite crystal structure³⁴, we propose that the undesirable FA-based perovskite-
91 DMF complex intermediates, which originally transform into δ -phase perovskites, can be directly
92 converted to α -phase perovskite intermediates with the addition of MACl. From the *in situ* XRD
93 studies, we inferred the corresponding nucleation and growth behaviors with the further introduction
94 of MACl as illustrated in **Fig.1b**. In addition, the MACl can also induce higher orientation growth
95 of perovskite crystals, resulting in high-quality perovskite films. By further passivating defects
96 around the crystals by excess PbI₂ and forming two-dimensional (2D) perovskite with the long-
97 chain ligands on the three-dimensional (3D) perovskite surface, a champion efficiency of 24.02%
98 is achieved on small-sized PSCs. With precise control of geometrical fill factor (~96%) for solar
99 modules, the corresponding 5 cm \times 5 cm solar mini-module demonstrates high efficiency of 20.5%
100 on an aperture area of 22.4 cm², corresponding to an active area efficiency of 21.4% and a total area
101 efficiency of 18.4% on a 25.0 cm² substrate. More importantly, this strategy can be also translated
102 to even larger scales by scalable printing, enabling a fully blade coated 15 cm \times 15 cm solar sub-
103 module with high efficiency of 15.3% on an aperture area of 205 cm².

104 **Self-drying FA-Cs perovskite ink modulation**

105 We firstly optimized the nucleation and growth processes of the narrower bandgap perovskite
106 material, FA_{0.88}Cs_{0.12}PbI₃, for satisfying the commercial scaling-up printing process. However, at
107 low concentrations of Cs, the intrinsic properties such as formation energy, morphology, and
108 especially the crystallization process would be significantly changed as presented in
109 **Supplementary Fig 1**. Even by further introduction of 10% molar ratio PbCl₂ into the perovskite
110 precursor as described in our previous work²⁴, it is still not enough to eliminate the pinholes in the
111 FA_{0.88}Cs_{0.12}PbI₃ perovskite film even after anti-solvent-free spin-coating (**Supplementary Fig. 2**).
112 To gain further knowledge, the pure FA_{0.88}Cs_{0.12}PbI₃ perovskite film was self-dried on the FTO
113 substrate from the NMP/DMF co-solvent system at room temperature. We observed a poor
114 morphology with a lot of rectangular bulk clusters stacking on top of one another (**Fig. 2a**,
115 **Supplementary Fig. 3**), which was induced by the formation of stronger FA₂Pb₃I₈•4DMF
116 intermediates than the PbI₂•NMP adducts, as demonstrated in the *in situ* XRD results (**Fig. 2b**).
117 Therefore, the strong competitiveness of the DMF solvent-coordinated perovskite complex
118 intermediates during the nucleation process contributes to the poor morphology of the final

119 perovskite films.

120 To further suppress the perovskite-DMF complex intermediates, instead of introducing excessive
121 PbCl_2 (**Supplementary Fig. 2**), we find that they can be completely suppressed by the introduction
122 of MACl, and most of which leaves the perovskite film eventually and does not substantially enlarge
123 the optical bandgap of perovskite³⁴. By introducing the MACl with a molar ratio of 0.3 to the
124 stoichiometric perovskite precursor, more nuclei form with smaller cluster size as shown in **Fig. 2c**.
125 The $\text{FA}_2\text{Pb}_3\text{I}_8 \cdot 4\text{DMF}$ intermediates that would originally transform to δ -phase are completely
126 suppressed based on the *in situ* XRD study (**Fig. 2d**). More interestingly, the α -phase perovskite
127 directly forms and becomes predominant at the expense of the δ -phase during solvent evaporation.
128 Even without the assistance of NMP, which helps lower the free energy^{24,37}, the α -phase perovskite
129 also forms in the pure DMF system with the addition of MACl additives (**Supplementary Fig. 4**).
130 This fast formation of α -phase perovskite can be ascribed to the lower formation energy by the
131 incorporation of MACl as demonstrated from the theoretical calculation results (**Fig. 2e**,
132 **Supplementary Fig. 5**), which confirms that MACl has been preferentially incorporated into the
133 FAPbI_3 perovskite crystal structure than the majority of CsI during the initial crystallization process
134 and thus stabilizes the formation of α -phase (black phase) firstly. Therefore, the undesirable growth
135 of $\text{FA}_2\text{Pb}_3\text{I}_8 \cdot 4\text{DMF}$ intermediates from the pristine precursor ink can be directly converted into the
136 α -phase perovskite intermediates with the addition of MACl, as depicted in the schematic **Fig. 1b**,
137 which improves the competitiveness of $\text{PbI}_2 \cdot \text{NMP}$ adducts and suppresses the undesirable δ -phase
138 formation, contributing to a denser morphology. As a result, a much denser film can be obtained
139 after self-drying at room temperature as shown in the SEM images (**Fig. 2f**).

140 **Self-driven compact FA-Cs perovskite during ripening**

141 Thermal annealing at different temperatures is employed to observe the crystal growth and
142 corresponding morphology changes. **Fig. 2f** shows the SEM images of the self-dried films with
143 MACl additives after thermal annealing at different temperatures. As the temperature increases,
144 smaller grains fuse into one larger grain and the holes disappear, while simultaneously the solvent
145 and MACl (or their byproducts) are volatilized, as confirmed by the mass spectroscopy analysis
146 (**Supplementary Fig. 6**), which suggest that the overall mechanism is consistent with a typical
147 Ostwald ripening process, as depicted in **Fig. 3a**. A pinhole-free compact perovskite film with
148 micro-sized grains and high crystallinity is readily obtained after thermal annealing at 150 °C,

149 however, a further increase in temperature would lead to the rapid decomposition of perovskite into
150 PbI_2 due to the volatilization of FA (**Supplementary Fig. 7a-b**). In sharp contrast, without MACl
151 additives, the perovskite film shows small size grains and conspicuous pinholes (**Supplementary**
152 **Fig. 3b**). This indicates that the introduction of MACl can induce the formation of a compact film
153 easily from the self-drying precursor ink after ripening.

154 To reduce the surface roughness caused by the non-uniform solvent evaporation under self-drying,
155 we find that a simple spin-coating process is suitable to deposit a smoother and denser film with
156 much smaller nuclei. Furthermore, a highly orientated perovskite film with compact morphology
157 and smooth surface is easily achieved by this MACl induced Ostwald ripening process, while the
158 pristine counterpart (without MACl) from the anti-solvent free spin-coating still presents poor
159 crystallinity and obvious pinholes even after thermal annealing (**Fig. 3b-c, Supplementary Fig. 11**).
160 To further understand the crystal growth behavior during the Ostwald ripening process with MACl
161 additives, the XRD characterization was conducted for the spin-coated films after thermal annealing
162 at different temperatures as shown in **Supplementary Fig. 7**. A new diffraction peak appeared at
163 9.3° under low-temperature annealing, which is possibly a mixed MACl and Cs-based new phase
164 perovskite as demonstrated by the XRD results (**Supplementary Fig. 8**). Then, this peak
165 disappeared when the temperature was over 75°C due to the volatilization of MACl as confirmed
166 by the mass spectroscopy results (**Supplementary Fig. 6**), leading to a blend structure of Cs and
167 FA-based perovskite after the removal of MACl, and subsequently generating the FA-Cs-mixed
168 cations-based perovskite films. Therefore, the crystallization process can be described by the two
169 paths as shown in **Supplementary Fig. 9**. One path forms the stable PbI_2 -NMP adducts, and the
170 other path which would originally form the perovskite-DMF complex intermediates is directly
171 converted into α -phase $(\text{MAFACs})\text{Pb}(\text{ICl})_3$ perovskite intermediates with the insertion of MACl.
172 With the further volatilization of NMP during the ripening process, some of the released PbI_2 can
173 react with the residual FAI, CsI and MACl to form this new intermediate phase and α -phase
174 $(\text{MAFACs})\text{Pb}(\text{ICl})_3$ perovskite intermediates under low temperature. Finally, the mixed cations-
175 based perovskite $(\text{FA}_{0.88}\text{Cs}_{0.12}\text{PbI}_3)$ structure forms due to the release of MACl under higher
176 temperature ripening, which suppresses the δ -phase formation during the whole growth process.

177 More importantly, this MACl induced cation and anion exchange during the crystallization
178 process not only improves the morphology but also stabilizes the α -phase FA-Cs perovskite films.

179 Even without thermal annealing, the nuclei formed in the MACl-added films continue to grow into
180 larger size polygonal grains with micron size (**Supplementary Fig. 10**). The results also
181 demonstrated the formation of a stable α -phase and no δ -phase even after 60 min in the ambient
182 environment (temperature ~ 25 °C, relative humidity $\sim 50\%$), while the films without MACl still
183 remain small crystals and are converted to δ -phase directly (**Supplementary Fig. 10**). Therefore,
184 this growth strategy is potentially suitable for the scalable fabrication of large-size perovskite films
185 in an ambient environment.

186 **Defect modulation**

187 To further improve the quality of perovskite films, we employ a simple passivation strategy for
188 the grain boundaries, by introducing proper excess PbI_2 (5% molar ratio) in the precursor ink
189 according to previous reports³⁸, and post-treatment with organic salts (dodecylamine hydrobromide,
190 DABr) to passivate both the boundaries and surface of the grains, respectively. The corresponding
191 crystallinity and morphology changes are shown in **Fig. 3b-f and Supplementary Fig. 11**. The
192 solubility of MACl in the stoichiometric perovskite ($\text{FA}_{0.88}\text{Cs}_{0.12}\text{PbI}_3$) precursor solution can be also
193 improved by the reaction with the introduced excess PbI_2 , which avoids the formation of flocculent
194 precipitates with Cs precursors (**Supplementary Fig. 12**). The post-treatment of DABr will form a
195 2D layer perovskite by the reaction with the introduced excess PbI_2 or cations exchange due to the
196 isopropanol (IPA) solvent that can slightly dissolve some of the FA molecules and thus enlarge the
197 bandgap of the perovskite films (**Supplementary Figures 13 and 14**). The resulting 2D layer serves
198 as a superhydrophobic protective layer with a large water contact angle over 90° due to the long
199 carbon chain (**Supplementary Fig. 13j**), and thus it would greatly improve the stability of the
200 corresponding devices.

201 To visualize the defect passivation effect through the above strategies, the time-resolved confocal
202 PL microscopy measurement was performed to characterize the charge carrier lifetime of these
203 perovskite films in microdomain ($10\ \mu\text{m} \times 10\ \mu\text{m}$) as shown in **Fig. 3g-j**. There was no obvious
204 difference in the lifetime of perovskite films with or without MACl additives, both of which show
205 a uniform green region. But it can be seen that the brighter grains and darker boundaries are clear
206 for the film with MACl additives. After the introduction of excess PbI_2 , the dark boundaries transit
207 to a light red color with a longer PL lifetime, indicating that the excess PbI_2 could passivate the
208 grain boundaries effectively. Moreover, the post-treatment of the perovskite film with DABr turns

209 a relatively large fraction of the film into a red and yellow-colored region, which means that the PL
210 lifetime is greatly enhanced. These results indicate that this series of processes can effectively
211 passivate the perovskite grains and/or surface to reduce the trap-induced or non-radiative
212 recombination in the films, which would be beneficial to improve the performance of the
213 corresponding devices.

214 **Antisolvent-free spin-coated solar cells**

215 To evaluate the photovoltaic performance of these perovskite films through the above strategies, a
216 standard structure of FTO/SnO₂/perovskite/spiro-OMeTAD/Au is employed as shown in the energy
217 level diagram (**Supplementary Fig. 15**), which exhibits a more preferable energy level alignment
218 for charge transport with the bulk and surface passivation. The champion *J-V* curves of the
219 corresponding devices based on these different spin-coated perovskite films without the use of anti-
220 solvent are shown in **Fig. 4a**. The pristine device with the FA_{0.88}CS_{0.12}PbI₃ perovskite as the light
221 absorber layer exhibits a relatively low efficiency of 18.99% with large hysteresis. With the
222 modulation induced by MACl, a significantly improved efficiency of over 22% is achieved. The
223 efficiency can be further improved to over 23% by the introduction of excess PbI₂. Finally, after the
224 post-treatment with DABr, much higher efficiency of close to 24% was achieved, mainly because
225 *V*_{oc} was dramatically improved by passivating the defects and subsequently reducing the charge
226 recombination. All the detailed parameters derived from the *J-V* curves are summarized in
227 **Supplementary Table 1**. The corresponding statistic distribution of photovoltaic parameters for
228 these different perovskite-based devices shows a clear improvement tendency by this series of
229 processing strategies (**Supplementary Fig. 16**). The typical steady-state output efficiencies for the
230 different devices are shown in **Supplementary Fig. 17**. However, the devices still show an obvious
231 hysteresis.

232 To further suppress the hysteresis, we introduced the KPF₆ additives in the precursor ink
233 according to our previous report²⁴. A champion efficiency of 24.02% is obtained for the optimized
234 device with negligible hysteresis (**Fig. 4b**). The corresponding integrated *J*_{sc} of 24.0 mA·cm⁻² from
235 external quantum efficiency (EQE) spectra matches well with the measured *J*_{sc} from the *J-V*
236 characterization (**Fig. 4c**). The typical devices also exhibit good light soaking stability and thermal
237 stability, which delivered an expectant T₈₀ lifetime over 1000 hours at MPP under one-sun
238 irradiation and an average ~90% efficiency retention after 20 days at 65 °C (**Supplementary Fig.**

239 **18**). We also demonstrate high-efficiency perovskite solar mini-modules on $5\text{ cm} \times 5\text{ cm}$ substrates
240 with a high geometrical fill factor ($\sim 96\%$) by the precise control of the P1-P2-P3 process
241 (**Supplementary Fig. 19**). The corresponding $5\text{ cm} \times 5\text{ cm}$ solar mini-module demonstrates a high
242 efficiency of 20.5% on an aperture area of 22.4 cm^2 , which corresponds to an active area efficiency
243 of 21.4% and a total area efficiency of 18.4% on a 25.0 cm^2 substrate, respectively (**Fig. 4d**).

244 **Scalable printed solar sub-modules**

245 Scalability and stability are currently the two major obstacles to realizing the commercial
246 application of perovskite solar cells. By the modulation of self-drying FA-Cs perovskite ink through
247 this series of strategies, a large-area high-quality and stable perovskite film can be blade coated in
248 a simple glovebox with a rough control of the local atmosphere (temperature = $15 \pm 5\text{ }^\circ\text{C}$; relative
249 humidity = $15 \pm 5\%$, where a lower temperature is helpful to initiate the crystallization process after
250 formation of uniform nuclei³⁹ and lower humidity is helpful to facilitate the nucleation process, and
251 thus contributes to a denser and smoother morphology as shown in **supplementary Fig. S20 and**
252 **Supplementary Note 2**). **Fig. 5a** illustrates the printing of large-size perovskite films by a blade
253 coating setup with an additional gas-assisted drying system, which enables fast and homogenous
254 volatilization of the host solvent and results in a uniform and dark black large-area perovskite film.
255 Characterization results performed on 5 different locations on the large-area $15\text{ cm} \times 15\text{ cm}$
256 perovskite film indicate that the scalable printed film is of a high level of uniformity
257 (**Supplementary Fig. 21**). By contrast, without the modulation of the precursor ink, the large-area
258 film shows a porous feature (**Supplementary Fig. 22**).

259 Then we used the blade coated high-quality large-area perovskite films to fabricate $15\text{ cm} \times 15\text{ cm}$
260 perovskite solar sub-modules, which is only limited by the processing scale of our laser machine
261 and evaporation system. A uniform purple color spiro-OMeTAD film is achieved on the top of this
262 uniform perovskite substrate by blade coating (**Supplementary Fig. 23a-b**). The cross-sectional
263 SEM image of the perovskite solar module shows a uniform perovskite layer with micro-size grains
264 sandwiched by a uniform spiro-OMeTAD layer and a thin SnO_2 layer (**Fig. 5b** and **Supplementary**
265 **Fig. 23c**). The photographs and design of the P1-P2-P3 pattern of a $15\text{ cm} \times 15\text{ cm}$ perovskite solar
266 sub-module are shown in **Supplementary Fig. 24**. By these strategies, a champion efficiency of
267 15.3% is obtained for a $15\text{ cm} \times 15\text{ cm}$ perovskite solar sub-module containing 21 sub-cells with an
268 aperture area of 205 cm^2 as shown in **Fig. 5c**. **Supplementary Fig. 25a and b** show the typical

269 reverse scan (RS) and forward scan (FS) of a large 15 cm × 15 cm perovskite solar sub-module, as
270 well as the output current density under maximum power point. **Supplementary Fig. 25c** shows the
271 efficiency distribution of 15 cm × 15 cm perovskite solar sub-modules that were fabricated on
272 different days. The module efficiencies from different upscaling methods with different aperture
273 areas over 150 cm² are summarized in **Supplementary Fig. 25d** and **Supplementary Table 2**. The
274 photovoltaic conversion efficiency of the high-quality perovskite films obtained in this work using
275 intermediate phase-modulated strategies is relatively higher than all other reported works, within
276 comparable size and printing technology, indicating the great promise for scalable printing of large-
277 size perovskite solar panels. To further understand the PCE difference between the small area cells
278 and sub-modules and their origins, we measured the J-V curves of the small cells (**Supplementary**
279 **Fig. 25 e-f, Supplementary Table 4**), which were cut at 5 different locations from a 15 cm × 15 cm
280 sub-module. The relatively small difference in PCE between the separately prepared small cells
281 (PCE ~ 24%) and the small cells cut from the 15 cm × 15 cm sub-module (PCE ~ 21%) indicates
282 that the relatively large PCE difference between the separately prepared small cells (PCE ~ 24%)
283 and the 15 cm × 15 cm sub-modules (PCE ~ 15%) is due to not only film uniformity issues when
284 upscaling solar cells from small areas to large areas and fabrication environmental condition
285 differences between small cell fabrication and large area sub-module fabrication, but also other
286 factors (such as sheet resistance of FTO substrates, issues related to laser scribing, etc.).

287 In addition, we also characterized the operational stability of the solar mini-module as shown
288 in **Fig. 5d** and **Supplementary Fig. 26**, which exhibited a T₈₀ lifetime over 1000 hours at MPPT
289 under one-sun irradiation. The initial output PCE of 19.2% is consistent with the efficiency (19.5%)
290 derived from the *J-V* curve (**Fig. 5e, Supplementary table 3**). Interestingly, although the efficiency
291 of the mini-module dropped to 15.3% after exposure to light for over 1000 hours, it almost reversibly
292 recovered to 19.1% after storage in dark. Therefore, this modulation strategy of the FA-Cs
293 perovskite precursor ink provides a promising technology for scalable manufacturing of efficient
294 and relatively stable large-scale perovskite solar modules.

295 **Conclusion**

296 In summary, we report an efficient upscaling fabrication strategy of high-quality and stable FA-Cs
297 perovskite films by modulating crystal growth from the self-drying precursor ink without the use of
298 anti-solvent. The obstacles in the formation of high-quality FA_{0.88}Cs_{0.12}PbI₃ perovskite films have

299 been overcome *via* this strategy through the addition of MACl in the co-solvent system of N,N-
300 dimethylformamide (DMF)/ N-methyl-2-pyrrolidone (NMP), which dramatically lower down the
301 formation energy and enlarge the crystal size of the perovskite films, contributing to scalable
302 deposition of large-area high-quality stable perovskite films successfully. For small-sized solar cells,
303 a high efficiency of 24.02% is achieved by further passivation of both the grain boundaries and
304 surface *via* an *in situ* formed excess PbI_2 and the corresponding formed 2D capping layer, as well
305 as the KPF_6 additives. For solar mini-modules, a relatively high efficiency of 20.5% on an aperture
306 area of 22.4 cm^2 with a high geometrical fill factor of 96% is demonstrated for a $5 \text{ cm} \times 5 \text{ cm}$ solar
307 mini-module. For large-scale solar sub-modules fabricated by a blade coating technique, a champion
308 efficiency of 15.3% with an aperture area of 205 cm^2 is demonstrated. In addition, the solar mini-
309 modules exhibit impressive stability with a T_{80} lifetime over 1000 hours at MPPT under one-sun
310 illumination. We expect that our modulation strategy of the precursor ink will pave the way towards
311 the commercial production of high-performance and stable perovskite solar modules in the near
312 future.

313 **Methods**

314 **Materials.** All reagents were used as received without any further purification, including CsI
315 (99.999% trace metals basis, Sigma Aldrich), PbI_2 (99.99%, TCI), formamidinium iodide (FAI,
316 Xi'an Polymer Light Technology Corp.), methylammonium chloride (MACl, Xi'an Polymer Light
317 Technology Corp.), 2,2',7,7'-tetrakis[N,N-bis(p-methoxyphenyl) amino]-9,9'-spirobifluorene
318 (spiro-OMeTAD, 99.8%, Xi'an Polymer Light Technology Corp.), 4-tert-butylpyridine (99.9%,
319 Sigma-Aldrich), bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI, Sigma-Aldrich), FK209
320 Co(III) TFSI salt (Sigma-Aldrich), acetonitrile (99.9%, Sigma-Aldrich), chlorobenzene (99.8%,
321 Wako), potassium hexafluorophosphate (KPF_6 , Sigma-Aldrich), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (99.99%, Sigma-
322 Aldrich), urea (Sigma-Aldrich), thioglycolic acid (Sigma-Aldrich), HCl (Wako), N,N-
323 dimethylformamide (DMF, Wako), 1-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich),
324 dodecylamine hydrobromide (DABr, TCI), isopropanol (IPA, Wako).

325 **Precursor solution preparation.** The different perovskite precursor solutions were prepared based
326 on a stoichiometric composition of $\text{FA}_{0.88}\text{Cs}_{0.12}\text{PbI}_3$ -NMP perovskite materials dissolved in DMF
327 solvent with further addition of the different amounts of MACl, PbI_2 , and KPF_6 (with molar ratio to
328 perovskite as mentioned in the main text file. If we wake the $\text{FA}_{0.88}\text{Cs}_{0.12}\text{PbI}_3$ -0.3MACl-NMP/DMF

329 solution as the example, 151.4 mg FAI, 31.2 mg CsI, 461 mg PbI₂, 20.3 mg MACl and 96 uL NMP
330 are dissolved in 500 uL DMF to form the precursor solution). The spiro-OMeTAD solution was
331 prepared by dissolving 90 mg spiro-OMeTAD in 1 mL chlorobenzene, adding 21 uL Li-TFSI (from
332 520 mg mL⁻¹ stock acetonitrile solution) and 11 uL FK209 (300 mg mL⁻¹ stock acetonitrile solution)
333 and 35 uL 4-tert-butylpyridine.

334 **Small-size perovskite solar cell fabrication.** The FTO glass was firstly etched using a laser scribe
335 machine. Then it was cleaned through ultrasonic cleaning by detergent, pure water, and ethyl alcohol
336 for 20 min, respectively. After drying by dry-air blowing, it was treated by UVO for 15 min before
337 use. The SnO₂ layer was deposited onto a clean FTO substrate of different sizes by a chemical bath
338 deposition (CBD) method²⁴. Then a 2 M FA_{0.88}Cs_{0.12}PbI₃-NMP/DMF perovskite precursor solution
339 with further addition of different additives was simply spin-coated onto SnO₂/FTO substrates in an
340 N₂-filled glovebox (temperature ~15 °C; relative humidity <5%) at 5000 rpm for 60 s, respectively.
341 Then the films were annealed at 70 °C for 1 min and taken out for further annealing at 150 °C for
342 10 min in an ambient environment with a relative humidity of 20~30%. All the achieved perovskite
343 films were treated with 15 mM DABr/IPA solution at 4000 rpm for 20 s, and then annealed at 100 °C
344 for 5 min. The spiro-OMeTAD solution was spin-coated on the perovskite films at 4000 rpm for 20
345 s. Finally, 80-nm thick of gold was deposited using thermal evaporation to complete the whole
346 device.

347 **5 cm × 5 cm perovskite solar mini-module fabrication.** The designated P1 pattern of FTO glass
348 is customized from the Yingkou OPV Tech New Energy Co., Ltd as depicted in Supplementary Fig.
349 19. Then it was cleaned and deposited with the SnO₂ layer as described above. The perovskite films
350 were spin-coated onto the 5 cm × 5 cm substrates and annealed according to the above procedures.
351 It should be noted that it is better to use a gas-assisted method to remove large amounts of volatile
352 DMF gas immediately. Otherwise, it will react with the dry film and affect the nucleation process.
353 After the treatment with DABr and spin-coating of spiro-OMeTAD films, the samples were etched
354 by a picosecond laser (Picosecond Laser Processing System, LPS-R002A, Spectronix Corporation.
355 The laser wavelength is 532 nm and the pulse duration is 12 ± 3 ps to form a P2 pattern (the used
356 power is 3.0 W and the average fluence per pulse is ~0.23 J cm⁻² pulse⁻¹) and to subsequently form
357 a P3 pattern (the used power is 3.8 W and the average fluence per pulse is ~0.29 J cm⁻² pulse⁻¹)
358 according to Supplementary Fig. 19 after evaporation of gold electrodes.

359 **15 cm × 15 cm perovskite solar sub-module fabrication.** The designated P1 pattern of FTO glass
360 is depicted in Supplementary Fig. 24. Then it was cleaned and deposited with the SnO₂ layer as
361 described above. The 1.25 M perovskite precursor ink were blade coated onto the 15 cm × 15 cm
362 substrates in a simple glovebox with a rough control of the local atmosphere (temperature = 15 ±
363 5 °C; relative humidity = 15 ± 5%) and then Then the films were taken out for annealing at 70 °C
364 for 1 min and further annealing at 150 °C for 10 min in an ambient environment with relative
365 humidity 20~30%. The perovskite precursor ink was manually supplied to the coater head during
366 the coating process. The distance between the blade coater head and the substrate was 0.35 mm (Z
367 =0.35 mm). The motor rotation frequency for the blade coating process was set as 500 Hz,
368 corresponding to a coating speed of ~ 3 mm/s. The angle between the air knife and substrate was
369 about 60°. The N₂-gas pressure was set at ~0.3 MPa. Then a 5 mM DABr/IPA solution was blade
370 coated onto the perovskite substrates accordingly, which was followed by thermal annealing at 100 °C
371 for 5 min. The spiro-OMeTAD solution was also blade coated onto the substrates accordingly. The
372 samples were etched by a picosecond laser to form a P2 pattern and etched again to form a P3 pattern
373 according to Supplementary Fig. 24 after evaporation of the gold electrode.

374 **Photovoltaic performance characterization.** The I - V characteristics of the perovskite solar cells
375 were measured using a Keithley 2420 source meter in the dry room (temperature = 15 ± 5 °C, relative
376 humidity = 25 ± 5 %). The light source is a solar simulator (Newport Oriel Sol 1A, xenon lamp,
377 USHIO, UXL-150SO) to match AM 1.5 G. The intensity of the light is 100 mW cm⁻² calibrated by
378 using a KG3 reference silicon cell (Enlitech). The EQE spectra were measured by using Oriel IQE
379 200. All the devices were tested using a black metal mask with an aperture area of 0.16 cm² for the
380 small devices and 22.4 cm² for the 5 cm × 5 cm mini-modules and 205 cm² for the 15 cm × 15 cm
381 sub-modules, respectively. The I - V scan range was from -0.1 to 1.2 V for the small-size solar cells
382 and from -0.1 to 8.5 V for the mini-modules and from -0.5 to 25 V for the sub-modules. The
383 corresponding I - V (or J - V) curves were measured at scan rates of ~0.2 V s⁻¹ for the small-area solar
384 cells, ~0.8 V s⁻¹ for the 5 cm × 5 cm mini-modules and ~2.0 V s⁻¹ for the 15 cm × 15 cm sub-modules
385 respectively without preconditioning.

386 **Light stability testing.** The perovskite solar cells under maximum power point (MPP) and mini-
387 modules under maximum power point tracking (MPPT) were tested in our home-designed
388 environmental enclosure box under a flow of dry N₂ to keep the relative humidity below 5%

389 (Supplementary Fig. 26). The devices were illuminated by a solar simulator (PEC-L01, Peccel) and
390 the power output was measured continuously using a source meter (Keithley 2401) controlled by a
391 program written in Labview. The algorithm used for MPPT is based on perturbation-observation. It
392 starts by applying the maximum voltage derived from the first I - V curve (Fig. 5d), then the applied
393 voltage is perturbed every minute with a small voltage variation to search for maximum power point,
394 and the corresponding maximum voltage, maximum current and maximum power are recorded.

395 **Characterization.** The surface morphologies of the perovskite films and the cross-sectional
396 structure of the PSCs were investigated using scanning electron microscopy (FEI Quanta 250 FEG
397 FEI Quanta 250 FEG). The UPS and XPS measurements were conducted by using an X-ray
398 photoelectron spectrometer (AXIS Ultra HAS, Kratos) equipped with monochromatic Al $K\alpha$
399 (1,486.6 eV) and non-monochromatic HeI (21.22 eV) sources. X-ray diffractometer (XRD, Bruker
400 D8 Discover), UV-vis spectrometer (V-670, JASCO), Time-resolved confocal PL microscopy
401 (Micro Time 200, PicoQuant GmbH), Mass spectrometry (HAL 3F-510, Hiden Analytical), were
402 used for the characterization of perovskite films, respectively. The atomic force microscopy
403 topography images in Supplementary Fig. 11b were acquired by an atomic force microscope (Model:
404 Park NX10) in the non-contact mode using a Si cantilever with a nominal spring constant of 42 N
405 m^{-1} (Model: PPP-NCHR). The atomic force microscopy topography images in Supplementary Fig.
406 20e, Supplementary Fig. 21d and Supplementary Fig. 22d were acquired by an atomic force
407 microscope (Model: Asylum Research MFP-3D) in the tapping mode using a Si cantilever with a
408 nominal spring constant of 48 N m^{-1} (Model: Budget Sensors Tap190Al-G).

409 **Computational methods.** All calculations were carried on the basis of projector-augmented wave
410 method as implemented in the Vienna *ab initio* simulation package (VASP) code⁴¹⁻⁴³. Perdew-
411 Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was
412 employed to describe the exchange-correlation interaction⁴⁴. Van der Waals correction proposed by
413 the Grimme potential (D2) was considered⁴⁵. The plane-wave basis cutoff energy was set to be 400
414 eV. The Monkhorst-Pack k-point mesh was sampled with a separation of about 0.015 \AA^{-1} in the
415 Brillouin zone. All structures were relaxed until the residual force on each atom was less than 0.01
416 eV/ \AA . The self-consistent convergence accuracy was set at 10^{-5} eV/atom in the structural calculation.
417 The numerical calculations in this paper have been done on the HPC system of Xidian University.
418 All the crystallographic information files (CIFs) of the structure models including α -

419 FAPbI₃(CCDC#1532918), δ -FAPbI₃(CCDC#968115), PbI₂(CCDC#77324), α -
420 CsPbI₃(CCDC#161481), δ -CsPbI₃(CCDC#161480), PbI₂·DMF (CCDC#1505389) and PbI₂·NMP
421 (CCDC#1915704) were obtained from the public database Cambridge Crystallographic Data Centre
422 (CCDC) via the website http://www.ccdc.cam.ac.uk/data_request/cif and references⁴⁶⁻⁴⁹.

423 **Data availability**

424 All data generated or analyzed during this study are included in the published article and its
425 Supplementary Information. Source Data and Supplementary Data are provided with this paper.

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432 **Author contributions**

433 Y.B.Q. supervised the project. Y.B.Q. and T.B. conceived the ideas. T.B. designed the experiments
434 and conducted the corresponding device and module fabrication and characterization. L.K.O.
435 contributed to part of the characterization and analyses. J.L. helped with the XRD and TRPL
436 mapping characterization. J.S. conducted the DFT calculations. G.T. helped with the stability test.
437 Y.B.Q. contributed to part of the AFM measurements in this study. J.Z. contributed to part of the
438 perovskite solar cell measurements in this study. Y.L., S.K., W.Z., J.C., F.H. and Y.-B.C. provided
439 valuable suggestions for the manuscript. Y.B.Q. and T.B. participated in all of the data analyses.
440 Y.B.Q. and T.B. wrote the paper, and all authors revised the paper.

441 **Competing interests**

442 The authors declare no competing interests.

443

444 **Figure Legends/Captions**

445 **Fig. 1. Solar sub-module configuration and intermediate phase-modulated growth strategy for**
446 **scalable deposition of the perovskite layer.** (a) Classifications of perovskite solar modules defined
447 by the area⁴⁰, and schematic illustration of the scalable fabrication of the perovskite solar sub-
448 module (The legend on the left hand side describes each functional layer, and the corresponding

449 scalable fabrication methods of each layer are described on the right hand side. P1-P2-P3: three
450 parting lines in a module). (b) Schematic illustration of the phase transition during the insertion and
451 removal of MAI. The initial competition between the perovskite-DMF complex intermediates and
452 PbI_2 -NMP adducts is suppressed by the conversion of perovskite-DMF complex intermediates to
453 MAI incorporated α -phase perovskite intermediates during crystallization, followed by the final
454 conversion to the α -phase perovskite with the release of MAI after the ripening process. Adapted
455 with permission.²⁴ Copyright 2021, AAAS.

456

457 **Fig. 2. Nucleation and growth process characterization of self-drying perovskite films.** (a, c)
458 Optical microscopy images and (b, d) *in situ* XRD patterns of the different perovskite inks self-dried
459 on the FTO substrates: (a, b) $\text{FA}_{0.88}\text{Cs}_{0.12}\text{PbI}_3$ -NMP/DMF and (c, d) $\text{FA}_{0.88}\text{Cs}_{0.12}\text{PbI}_3$ -0.3MAI-
460 NMP/DMF (purple circle, $\text{FA}_2\text{Pb}_3\text{I}_8 \cdot 4\text{DMF}$; solid green diamond, $\text{PbI}_2 \cdot \text{NMP}$; open diamond,
461 $\text{PbX}_2 \cdot 0.5\text{NMP} \cdot 0.5\text{DMF}$ ²⁴). (e) Schematic diagram of the formation energy changes of the
462 $(\text{FA}_{26/27}\text{Cs}_{1/27})\text{PbI}_3$ perovskite with the incorporation of MA and MAI, respectively ($x \leq 1/3$). The
463 horizontal grey dash line represents the baseline of energy (viz. the formation energy of pure
464 FAPbI_3), and the top sketches show the corresponding perovskite crystal structures, which are
465 viewed along the *c*-axis. (f) SEM images of the self-dried films from $\text{FA}_{0.88}\text{Cs}_{0.12}\text{PbI}_3$ -0.3MAI-
466 NMP/DMF precursor ink and the annealed films at different temperatures for 10 min.

467

468 **Fig. 3. Morphology and defect modulation.** (a) Schematic diagram of the Ostwald ripening, which
469 involves a phase transition of the MAI-induced perovskite intermediate (grey shape) and NMP-
470 induced $\text{PbI}_2 \cdot \text{NMP}$ solvate intermediate (yellow shape) to the final α -phase perovskite. (b) XRD
471 patterns of the spin-coated perovskite films with different additives after thermal annealing. (i)
472 $\text{FA}_{0.88}\text{Cs}_{0.12}\text{PbI}_3$ -NMP/DMF, (ii) $\text{FA}_{0.88}\text{Cs}_{0.12}\text{PbI}_3$ -0.3MAI-NMP/DMF, (iii) $\text{FA}_{0.88}\text{Cs}_{0.12}\text{PbI}_3$ -
473 0.05PbI_2 -0.3MAI-NMP/DMF, (iv) $\text{FA}_{0.88}\text{Cs}_{0.12}\text{PbI}_3$ -0.05 PbI_2 -0.3MAI-NMP/DMF with DABr
474 post-treatment. (c, d, e and f) SEM images and (g, h, i and j) time-resolved confocal PL mappings
475 of the corresponding perovskite films (i, ii, iii, and iv, respectively) after thermal annealing. Note
476 that the average carrier lifetime data (color scale bars) and the event count data (grey scale bars)
477 have been merged together in these images (g-j).

478

479 **Fig. 4. Photovoltaic performance characterization.** (a) Typical J - V curves of the devices based
480 on different perovskite films: (i) $\text{FA}_{0.88}\text{Cs}_{0.12}\text{PbI}_3$ -NMP/DMF, (ii) $\text{FA}_{0.88}\text{Cs}_{0.12}\text{PbI}_3$ -0.3MACI-
481 NMP/DMF, (iii) $\text{FA}_{0.88}\text{Cs}_{0.12}\text{PbI}_3$ -0.05 PbI_2 -0.3MACI-NMP/DMF, (iv) $\text{FA}_{0.88}\text{Cs}_{0.12}\text{PbI}_3$ -0.05 PbI_2 -
482 0.3MACI-NMP/DMF with DABr post-treatment. (b) J - V curves and (c) EQE spectrum of the
483 champion device with the KPF_6 additive. (d) I - V curves of the champion $5\text{ cm} \times 5\text{ cm}$ perovskite
484 solar mini-module with a series connection of 7-sub cells (PCE_{ap} is the aperture area efficiency and
485 PCE_{ac} is the active area efficiency.)

486

487 **Fig. 5. Scalable printing and stability characterization.** (a) Schematic illustration for the scalable
488 blade coating of large-area perovskite films. (b) Cross-section SEM image of the fully blade coated
489 perovskite solar sub-module. (c) I - V curve of the champion $15\text{ cm} \times 15\text{ cm}$ perovskite solar sub-
490 module (PCE_{ap} is the aperture area efficiency). Inset shows a photograph of the corresponding sub-
491 module with a series connection of 21-sub cells. (d) Operational stability test of a $5\text{ cm} \times 5\text{ cm}$
492 perovskite solar mini-module (aperture area = 22.4 cm^2) under maximum power point tracking
493 (unencapsulated device, in nitrogen atmosphere, at $\sim 30\text{ }^\circ\text{C}$) and (e) the corresponding I - V curves
494 before and after MPPT test and after dark storage.

495

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