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Research Article

# <sup>1</sup> Ionic Liquid-Assisted MAPbl<sub>3</sub> Nanoparticle-Seeded Growth for <sup>2</sup> Efficient and Stable Perovskite Solar Cells

<sup>3</sup> Md. Shahiduzzaman,<sup>\*,O</sup> LiangLe Wang,<sup>O</sup> Shoko Fukaya, Ersan Y. Muslih, Atsushi Kogo,

4 Masahiro Nakano, Makoto Karakawa, Kohshin Takahashi, Koji Tomita, Jean-Michel Nunzi,\*

s Tsutomu Miyasaka, and Tetsuya Taima\*



7 (PSCs), long-life operational stability has become a major requirement 8 for their commercialization. In this work, we devised a pristine cesium– 9 formamidinium–methylammonium (termed as CsFAMA) triple-cation-10 based perovskite precursor solution into the ionic liquid (IL)-assisted 11 MAPbI<sub>3</sub> nanoparticles (NPs) through a seeded growth approach in which 12 the host IL-assisted MAPbI<sub>3</sub> NPs remarkably promote high-quality 13 perovskite films with large single-crystal domains, enhancing the device 14 performance and stability. The power conversion efficiency (PCE) of the 15 MAPbI<sub>3</sub> NP-seeded growth of MAPbI<sub>3</sub> NPs/CsFAMA-based PSCs is as 16 high as 19.44%, which is superior to those of MAPbI<sub>3</sub> NPs and pristine 17 CsFAMA films as the photoactive layer (9.52 and 17.33%, respectively). 18 The long-term light-soaking and moisture stability of IL-aided MAPbI<sub>3</sub>



19 NPs/CsFAMA-based devices (non-encapsulated) remain above 90 and 80%, respectively, of their initial output after 2 h of light
20 illumination (1 sun) and 6000 h storage at ambient with a relative humidity range of 30–40%. The use of the IL-assisted MAPbI<sub>3</sub>
21 NP-seeded growth for PSCs is a significant step toward developing stable and reliable perovskite photovoltaic devices.

22 KEYWORDS: ionic liquid-assisted MAPbI<sub>3</sub> nanoparticle-seeded growth, dense perovskite, perovskite solar cells, stability

# 23 INTRODUCTION

24 Organometal halide perovskite solar cells (PSCs) are presently 25 the epitome of energy harvesting in photovoltaic materials. 26 Intensive research efforts all over the world have started in 27 2009 after Miyasaka.<sup>8</sup> The power conversion efficiencies 28 (PCEs) of PSCs (25.5%) in 2020 have approached or 29 exceeded those of other photovoltaic materials, such as silicon 30 (26.7%), copper indium gallium selenide solar cells (22.9%), 31 and cadmium telluride (22.1%).9 However, improvement of 32 the operational stability is necessary for PSC commercializa-33 tion.<sup>10-12</sup> Both extrinsic (environmental) and intrinsic factors 34 affect the PSC stability. Environmental factors such as 35 moisture, oxygen, and light or heat can damage the 36 photoactivity of PSCs.<sup>13,14</sup> The intrinsic stability of the 37 perovskite structure is affected by defects, both in the 38 perovskite film and at the interface between the perovskite 39 and charge transport layers.<sup>15</sup> Limited perovskite stability 40 originates from the hygroscopic nature of organic cations, 41 under-coordinated lead atoms, as well as ion migration and  $^{\rm 42}$  thermal degradation. The hygroscopic character can be  $^{\rm 43}$  remediated by encapsulation,  $^{\rm 16}$  and thermal stability can be 44 improved by engineering the perovskite composition and 45 inorganic hole-transport materials (HTMs).<sup>17-21</sup> Ion migra-46 tion in perovskite layers is an additional cause of PSC

degradation. Ion transport initiated by the electric field <sup>47</sup> induced by illumination can be reduced or even suppressed <sup>48</sup> by grain-boundary passivation through interface engineering.<sup>22</sup> <sup>49</sup> However, to realize the full potential of PSCs, simultaneous <sup>50</sup> improvement in device engineering needs to be considered. <sup>51</sup> Various materials have been added to the perovskite film, such <sup>52</sup> as polymers,<sup>23,24</sup> fullerenes,<sup>25</sup> metal halide salts,<sup>26</sup> organic <sup>53</sup> halide salts,<sup>27</sup> nanoparticles,<sup>28</sup> and ionic liquids (ILs),<sup>29–31</sup> <sup>54</sup> leading to highly efficient and stable PSCs. Among these <sup>55</sup> significant consideration as an additive, a solvent, an interface <sup>57</sup> modifier, and an independent electron transport layer (ETL) <sup>58</sup> for fabricating efficient and stable PSCs because of their high <sup>59</sup> thermal and electrochemical robustness, low-vapor pressure, <sup>60</sup> and high ionic conductivity.<sup>32</sup> Previously, we reported <sup>61</sup> imidazole-based IL in a MAPbI<sub>3</sub> precursor solution containing <sup>62</sup>

Received: January 12, 2021 Accepted: April 14, 2021



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63 only N.N-dimethylformamide (DMF) as a solvent and found 64 that uniform spherical MAPbI<sub>3</sub> nanoparticles (NPs) formed 65 after spin-coating. ILs allow rapid crystallization and formation 66 of uniform MAPbI<sub>3</sub> NPs. The resulting MAPbI<sub>3</sub> NPs were 67 used solely as a perovskite photoactive layer in PSCs.<sup>30,33,34</sup> 68 Seo et al.<sup>35</sup> fabricated a highly crystalline and uniform 69 perovskite film with large crystal domains by adding 70 methylammonium formate as an IL to the precursor, resulting 71 in champion planar PSCs with a stabilized power output of 72 19.5%. Wang et al.<sup>36</sup> reported water-soluble triazolium IL-73 induced perovskite, improving the stability and efficiency of 74 PSCs, maintaining an initial efficiency of around 80% for 3500 75 h under relative humidity and thermal conditions. Recently, 76 Bai and colleagues reported the use of IL in a triple-cation 77 perovskite precursor solution, increasing the efficiency and 78 long-term stability of the device,<sup>29</sup> which remained stable for 79 more than 1800 h under continuous simulated sunlight 80 exposure.

Over the last few years, the use of seeding growth offered an 81 82 attractive approach to aid the growth of high-quality perovskite 83 films, improving the PSC stability while maintaining its 84 efficiency. Li et al.<sup>37</sup> demonstrated an intermixing-seeded 85 growth technique for enhancing the device performance of 86 PSCs by adding a small amount of PbS NPs as the seed during 87 film formation. The authors stated that PbS NPs were capped 88 with methylammonium iodide precursor through interfacial 89 engineering with ligand exchange, which could function as 90 effective heterogeneous nucleation sites to promote the 91 perovskite lattice formation, consequently providing high-92 performance PSCs. Recently, Zhao et al.<sup>38</sup> reported a similar 93 concept of seeding growth approach that was applied to 94 modulate the perovskite crystallization by adding perovskite 95 seed crystals into a PbI<sub>2</sub> film. A perovskite seeding growth 96 approach was used to fabricate highly stable Cs-containing 97 FAPbI3-based PSCs, which retained over 60% of their initial 98 efficiency after 140 h at maximum power point under one sun 99 illumination. Zhang et al.<sup>39</sup> also produced a self-seeding growth 100 of high-performance PSCs with a PCE of 20.30%, retaining 101 80% of the original PCE over 4680 h storage at the ambient. 102 This self-seeding growth can be implemented by repeated 103 coating of a similar perovskite precursor solution. These 104 studies suggest that the beneficial effect of the seeding growth 105 approach facilitates fabrication of higher-quality perovskite 106 films, subsequently improving the efficiency and stability of the 107 resultant PSCs. As far as we know, despite significant progress 108 in the improvement of performance in the seeding growth-109 based PSCs, the use of IL-aided perovskite NP seeding growth 110 in the fabrication of higher-quality perovskite films with 111 remarkable PSC efficiency and stability has not been explored 112 yet.

In this study, we designed a novel technique in which the 114 pristine  $Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$  (termed as 115 CsFAMA) or pristine MAPbI<sub>3</sub> perovskite is grown by IL-116 assisted MAPbI<sub>3</sub> NP seeds to fabricate higher-quality perov-117 skite films with large crystal domains, subsequently improving 118 the efficiency and stability of the devices. Notably, the short-119 circuit density ( $J_{sc}$ ) improved in the CsFAMA or MAPbI<sub>3</sub> 120 devices embedded with NPs using the MAPbI<sub>3</sub> NP seeding 121 approach. To produce dense perovskite films, we dropped a 122 neat CsFAMA precursor solution on a wet film of the as-123 deposited IL-assisted MAPbI<sub>3</sub> NP clusters. The perovskite 124 nuclei with fewer seed clusters regrow during crystallization, 125 leading to the improvement in structural and optoelectronic 140

properties. We show that the use of a flat and dense perovskite 126 film with high crystallinity and large domain size leads to more 127 efficient charge carrier collection and thus better photovoltaic 128 performances. In addition, this strategy enables a significant 129 improvement in operational stability. Encouragingly, a highly 130 hydrophobic perovskite surface was achieved using the ILsignificantly improved the light-soaking and moisture stability. 133 Interestingly, also in the moisture stability, IL-aided MAPbI<sub>3</sub> 134 NPs/CsFAMA-based devices retained around 80% of the 135 initial characteristics after 6000 h storage at ambient under 136 30–40% humidity. More importantly, a similar trend with the 137 MAPbI<sub>3</sub> NPs/MAPbI<sub>3</sub> structure-based PSCs was observed for 138 the light-soaking stability. 139

#### **EXPERIMENTAL METHODS**

**Materials.** Fluorine-doped tin oxide (FTO)-coated glass was 141 purchased from Asahi Glass (Tokyo, Japan). 1-Hexyl-3-methylimida- 142 zolium chloride (HMImCl, 97% purity), chlorobenzene (CB), 143 titanium di-isopropoxide bis-(acetylacetonate) Ti(acac)<sub>2</sub>(OiPr)<sub>2</sub>, 144 and isopropanol (IPA) were purchased from Sigma-Aldrich (St. 145 Louis, MO). 2-Propanol (99.9% purity) was purchased from Wako 146 Pure Chemical (Tokyo, Japan). Methylammonium bromide (MABr), 147 methylammonium iodide (MAI), formamidinium iodide (FAI), 148 cesium iodide (CsI), lead bromide (PbBr<sub>2</sub>), and lead iodide (PbI<sub>2</sub>) 149 precursors were purchased from TCI (Tokyo, Japan). *N,N*- 150 Dimethylformamide (DMF, 99.5% purity) and dimethyl sulfoxide 151 (DMSO, 99.5% purity) were purchased from Wako Pure Chemical 152 (Tokyo, Japan). Spiro-OMeTAD (99.8% purity) was purchased from 153 Lumtec (New Taipei City, Taiwan).

Device Fabrication. A patterned FTO-glass substrate was 155 sequentially cleaned by sonication with a commercial detergent in 156 water, deionized water, acetone, and IPA for 15 min. The cleaned 157 FTO substrate was then nitrogen-dried and oxygen-plasma-treated for 158 20 min prior to use. A 40 nm thick TiO2 compact layer (CL) was 159 prepared on the FTO-glass substrate as follows. The TiO<sub>2</sub> CL was 160 spin-coated from 0.15 M Ti(acac)<sub>2</sub>(OiPr)<sub>2</sub> in 2-propanol at 2000 rpm 161 for 30 s, and the substrate was dried on a hot plate at 120 °C for 5 162 min. Two additional coatings with higher  $Ti(acac)_2(OiPr)_2$  solution 163 concentration (0.3 M) were performed at the same spinning 164 conditions (2000 rpm, 30 s) and dried at 120 °C for 5 min. The 165 substrate was further treated in a muffle furnace at 450 °C for 30 min. 166 The single-crystal brookite TiO<sub>2</sub> NPs were synthesized at pH 10 by 167 hydrothermal synthesis, as reported in our previous study.<sup>40</sup> The 168 brookite TiO<sub>2</sub> NP colloidal suspension was spin-coated at 2000 rpm 169 for 30 s on the TiO<sub>2</sub> CL and annealed for 5 min at 100 °C, followed 170 by three coating cycles (optimum condition), and finally baked at 180 171  $^\circ C$  for 60 min in a hot plate. The MAPbI3 perovskite NP films were 172 prepared following our previous report.  $^{30}$  The triple-cation-based 173 precursor solution with 5% Cs was prepared by mixing with FA/MA 174 in the DMF and DMSO (4:1) solvent mixture. The perovskite film 175 with a chemical formulation of  $Cs_x(FA_{0.83}MA_{0.17})_{(1-x)}Pb(I_{0.83}Br_{0.17})_3$ , 176 where the Cs fraction is x = 0.05 (Cs 5%), was fabricated.<sup>41</sup> The stock 177 solution of FAI (1 M), PbI<sub>2</sub> (1.1 M), MABr (0.2 M), and PbBr<sub>2</sub> (0.2 178 M) was mixed in anhydrous DMF/DMSO (4:1), and an appropriate 179 volume of CsI solution was added from the CsI stock solution (1.5 180 M) in DMSO to achieve 5% Cs solution. Prior to spin-coating, the 181 mixed precursor solution was stirred at 70 °C for 60 min. The mixed 182 perovskite solution was spin-coated in the following steps: first at 0 183 rpm for 10 s, second at 1000 rpm for 10 s, and third at 6000 rpm for 184 20 s. In the second step, 500  $\mu$ L of CB solvent was dripped 5 s before 185 the spin-coating stops. The samples were readily transferred to a hot 186 plate at 100 °C for 60 min. In addition, the pristine MAPbI<sub>3</sub> precursor 187 solution was prepared as described in our previous report.<sup>42</sup> A 188 precursor solution was prepared by dissolving spiro-OMeTAD, 189 lithium salt (9.1 mg), cobalt (8.7 mg), and 4-tert-butylpyridine 190 (28.8  $\mu$ L) in 1000  $\mu$ L of chlorobenzene under stirring at 800 rpm at 191 ambient for 6 h and used as the hole-transport layer (HTL). The as- 192

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**Figure 1.** Fabrication procedure of perovskite films using MAPbI<sub>3</sub> NP-based seeded growth. The inset shows the chemical structure of HMImCl (termed as IL), the AFM images of MAPbI<sub>3</sub> small clusters and MAPbI<sub>3</sub> NP film, and schematic of the molecular structure of the perovskite film and the mechanism of bonding configurations between the IL and the perovskite structure. Steps I–III of the fabrication procedure are described in the text.

<sup>193</sup> made spiro-OMeTAD precursor solution was spin cast at 4000 rpm <sup>194</sup> for 30 s on the perovskite film, and a 250 nm thickness was obtained. <sup>195</sup> Finally, the Au electrode was thermally evaporated at a thickness of <sup>196</sup> 100 nm on the HTL.

Characterization. Surface morphology was studied by field 197 198 emission scanning electron microscopy (FESEM; JEOL JSM-7610F, Tokyo, Japan). The chemical bonding state of the CsFAMA and 199 MAPbI<sub>2</sub> NPs/CsFAMA films was examined by X-ray photoelectron 200 spectroscopy (XPS) (JPS-9010MC, JEOL Ltd., Japan) with a non-201 monochromatic Mg K $\alpha$  source (photon energy: 1253.6 eV). The XPS 202 was analyzed in the constant energy mode at a 10 eV pass energy with 203 0.1 eV/step. The binding energy range was adjusted by setting the 204 lowest component of carbon (C) 1s (284.2 eV), which is the C 2.05 206 binding energy in aromatic compounds. Analysis of the resultant perovskite films was carried out using Fourier transform infrared 2.07 spectroscopy (FTIR) with infrared reflection absorption spectroscopy 2.08 (FT/IR-6300, Jasco, Tokyo, Japan). The structural properties of the 209 perovskite were monitored by X-ray diffraction (XRD) using an X-ray 210 diffractometer (SmartLab, Rigaku, Tokyo, Japan) with an X-ray tube 211 (Cu K $\alpha$  radiation,  $\lambda = 1.5406$  Å). The UV-vis absorption spectra of 212 perovskite films were measured using a Hitachi U-3310 (Tokyo, 213 214 Japan) absorption spectrophotometer. The charge transport properties of perovskites were characterized by photoluminescence (PL; FP-215 8600, Jasco Corporation, Tokyo, Japan) and electrochemical 216 impedance spectroscopy (EIS; E4980A Precision LCR Meter, Agilent, 217 Tokyo, Japan). AC IS measurements were conducted, and the 218 frequency range was set for the short-circuit mode with a 219 measurement amplitude of ±5 mV from 20 Hz to 1 MHz. The 220 measurement under light irradiation was performed using a solar light 2.2.1 simulator (SAN-EI Electric, Japan, XES-502S), producing artificial 2.2.2 sunlight of AM 1.5G, 100 mW/cm<sup>2</sup>. The current density versus 223 voltage (I-V) curves were measured at a scan rate of 0.05 V/s in 2.2.4 225 forward scan (FS; from -0.2 to 1.2 V) and reverse scan (RS; from 1.2  $_{226}$  to -0.2 V) configurations under simulated air mass (AM) 1.5G  $_{227}$  illumination using a solar simulator with 100 mW/cm<sup>2</sup> and a Keithley 228 2401 digital source meter. Every device had an active area of 0.09 cm<sup>2</sup>. 229 The incident photon-to-electron conversion efficiency (IPCE) spectra 230 were recorded using a monochromatic xenon arc light system 231 (Bunkoukeiki, SMI-250JA).

# RESULTS AND DISCUSSION

The fabrication of MAPbI<sub>3</sub> NPs/CsFAMA-based perovskite <sup>233</sup> films with embedded IL-aided MAPbI<sub>3</sub> NPs is schematized in <sup>234</sup> Figure 1. The inset shows the chemical structure of HMImCl <sup>235</sup> fI (termed as IL) and the mixed perovskite precursor solution. <sup>236</sup> Following our previous report (step-I in Figure 1),<sup>30</sup> we first <sup>237</sup> prepared a MAPbI<sub>3</sub> NP layer by adding a small amount of IL <sup>238</sup> into the perovskite spin-coating precursor solution. ILs are <sup>239</sup> known for their high-boiling point and extremely low-vapor <sup>240</sup> pressure, retarding the crystal formation and yielding <sup>241</sup> homogenous nucleation during the spin-coating process. <sup>242</sup>

MAPbI<sub>3</sub> small clusters grow during spin-coating, followed by 243 homogeneous nucleation to produce MAPbI<sub>3</sub> NPs (Figure 1, 244 step-I). The as-deposited MAPbI<sub>3</sub> forms NPs assembled into 245 small clusters with about 1  $\mu$ m size as evidenced by atomic 246 force microscopy (AFM) (Figure 1; inset). As shown in Figure 247 S1, upon annealing at 100 °C, the resultant IL-assisted MAPbI<sub>3</sub> 248 NPs are almost 200 nm size. The neat CsFAMA perovskite 249 precursor solution was spin cast on the wet film of IL-assisted 250 MAPbI<sub>3</sub> NP clusters (step-II). Importantly, ILs are nonvolatile 251 since their vapor pressure is close to zero. As shown in Figure 252 1, crystallization of the perovskite film grown on a wet film of 253 IL-assisted MAPbI<sub>3</sub> NP clusters involves two phases: 254 nucleation and crystal growth. Fewer clusters are left and act 255 as heterogeneous nucleation sites. This facilitates nucleation of 256 the final perovskite because the nucleation energy barrier for 257 crystal growth with seed clusters is lower than the one without 258 seeds.<sup>38</sup> Consequently, primary nucleation is dominated by the 259 MAPbI<sub>3</sub> small clusters. The grain morphology is affected by 260 the cluster's density during the crystallization process, which 261 slows down the crystal growth, producing densely embedded 262 MAPbI<sub>3</sub> NPs with larger perovskite crystal domains.<sup>35,36,43</sup> 263 Therefore, large crystal domains with fewer grain boundaries 264 are induced in the perovskite layer by IL-aided MAPbI<sub>3</sub> NPs 265 (step-III). This is one of the main reasons for the improved 266 stability of the PSCs. 267

As illustrated in Figure 1 (inset), based on the molecular 268 structure of the imidazolium IL and the two-dimensional 269



**Figure 2.** XPS spectra of the perovskite films formed with the CsFAMA and MAPbI<sub>3</sub> NPs/CsFAMA films: (a) Pb 4f and (b) I 3d. (c) FTIR spectra of the perovskite films formed with and without the MAPbI<sub>3</sub> NP film. (d) XRD spectra of the perovskite films formed with MAPbI<sub>3</sub> NPs, CsFAMA, and MAPbI<sub>3</sub> NPs/CsFAMA.

270 configuration of CsFAMA, there are several potential binding 271 configurations between the IL and the perovskite. XPS data show the interaction between the IL and the perovskite 272 involving methylimidazolium and hexyl chain as a head and tail 273 274 in 1-hexyl-3-methylimidazolium, respectively. As evident from XPS, the chloride with a negative charge in the IL tends to 275 276 bind to the Pb<sup>2+</sup> at the perovskite crystal. In addition, the 277 amino group with a lone electron pair in IL forms Pb-N bonds at the perovskite crystal. As shown in Figure 2a, the Pb 278 4f spectrum of the CsFAMA perovskite film exhibits two 279 characteristic peaks at 138.5 and 143.3 eV, corresponding to 280 the spin-orbit splitting of the Pb  $4f_{7/2}$  and  $4f_{5/2}$  constituents, 281 respectively. The resultant signals move to lower binding 282 energies of 138.3 and 143.1 eV, respectively, while using IL-2.83 assisted MAPbI<sub>3</sub> NPs as seeds embedded in the CsFAMA 284 structure, which confirms the coordination interaction between 285 the imidazolium ring and Pb<sup>2+</sup> defects.<sup>44,45</sup> Moreover, the I 3d 286 spectra shift upon the use of IL-assisted MAPbI<sub>3</sub> NPs from 287 619.3 to 618.2 eV (Figure 2b), suggesting an interaction 288 289 between the imidazolium and PbI3<sup>-</sup> defects and a reduced 290 interaction between I<sup>-</sup> and strongly electronegative Pb<sup>2+</sup>.

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<sup>291</sup> The presence of the IL also appears in the FTIR spectrum <sup>292</sup> (Figure 2c). The FTIR peaks at  $3700-3000 \text{ cm}^{-1}$  indicate the <sup>293</sup> free N-H bond from the IL that has a higher vibration energy

than the N-H bond in methylammonium that is trapped in 294 the perovskite structure. In addition, N-H peaks from the IL- 295 assisted sample are broadened, whereas N–H peaks from non- 296 IL sample are sharper. The broad peak at 3700-3000 cm<sup>-1</sup> 297 indicates N-H bonding in methylimidazolium, which under- 298 goes hydrogen bonding with halogens on the perovskite 299 surface, and these halogens are more likely to make a 300 coordination bonding with lead or with methylammonium, 301 formamidinium, and cesium that might have ended up on the 302 perovskite surface. Even, lead can end up at the surface due to 303 crystal defects. These elements are more likely positive active 304 sites for the IL. Thus, chloride as the negative charge of the IL 305 can bind with these positive sites. It finally ensures that the IL 306 is attached on the perovskite when the perovskite crystal has 307 formed completely. It can be concluded that the IL surrounds 308 the perovskite with head attached to the perovskite surface, 309 meanwhile the IL tail keeps off from the perovskite (Figure 1). 310 The resulting hydrophobicity may improve the IL-assisted 311 MAPbI<sub>3</sub> NP-embedded CsFAMA film, thus, increasing the 312 stability of the devices. 313

The XRD patterns of the MAPbI<sub>3</sub> NP, CsFAMA, and 314 MAPbI<sub>3</sub> NPs/CsFAMA films are shown in Figure 2d. The 315 peaks at 20.02, 24.52, and 26.57° significantly reduced and 316 shifted because some chloride could exchange with iodine in 317

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Figure 3. Top-view SEM images of the (a) MAPbI<sub>3</sub> NP, (b) CsFAMA, and (c) MAPbI<sub>3</sub> NPs/CsFAMA films. The grain size distribution histograms of the (d) MAPbI<sub>3</sub> NP, (e) CsFAMA, and (f) MAPbI<sub>3</sub> NPs/CsFAMA films.



Figure 4. (a) PL spectra of the MAPbI<sub>3</sub> NP, CsFAMA, and MAPbI<sub>3</sub> NPs/CsFAMA films on  $FTO/TiO_2$  CL/brookite  $TiO_2$  NPs. (b) Nyquist plots of MAPbI<sub>3</sub> NPs, CsFAMA, and MAPbI<sub>3</sub> NPs/CsFAMA-based PSCs. The inset shows the equivalent circuit model of the resultant devices. (c) TRPL spectra of CsFAMA and MAPbI<sub>3</sub> NPs/CsFAMA films on  $FTO/TiO_2$  CL/brookite  $TiO_2$  NPs.

318 the perovskite structure. Although it still reveals the perovskite 319 structure, the substitution can change the *d*-spacing. The 320 diffraction peaks at  $2\theta$  angles of 14.1 and  $28.4^{\circ}$  in the MAPbI<sub>3</sub> 321 NP, CsFAMA, and MAPbI<sub>3</sub> NPs/CsFAMA films correspond  $_{322}$  to the (110) and (220) crystal planes. The absence of the PbI<sub>2</sub>  $_{323}$  peak at  $12.6^{\circ}$  in all cases suggests the complete consumption of 324 PbI<sub>2</sub>. The full width at half-maximum (FWHM) of the (110) 325 diffraction peak is narrowed because of the incorporation of 326 MAPbI<sub>3</sub> NPs with the CsFAMA perovskite, indicative of the 327 larger perovskite crystal domains also visible in the SEM 328 images (Figure 3c). The FWHM of the peak decreases from 329 0.26 (CsFAMA) to 0.24 (MAPbI<sub>3</sub> NPs/CsFAMA) with 330 incorporation of the NP seeds. Lower FWHM also gives 331 evidence of the higher crystallinity of the MAPbI<sub>3</sub> NPs/ 332 CsFAMA films. Light absorption is slightly higher for the 333 MAPbI<sub>3</sub> NP-embedded CsFAMA film (Figure S2a). More 334 importantly, the overlapping spectra in the longer wavelength 335 area (near 770 nm) show that the band gap is unchanged.

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Figure 3a-c shows SEM images taken from the top of the 336 MAPbI<sub>3</sub> NP, CsFAMA, and MAPbI<sub>3</sub> NPs/CsFAMA films. 337 Smooth morphology and crystallinity of the perovskite films 338 enable efficient device performance and stability.<sup>46</sup> The 339 histograms of grain size distribution, along with Gaussian 340 fittings, are given in Figure 3d-f. The average grain sizes of 341 MAPbI<sub>3</sub> NP, CsFAMA, and MAPbI<sub>3</sub> NPs/CsFAMA films are 342 156, 380, and 572 nm, respectively. MAPbI<sub>3</sub> NPs with 343 spherical shape were obtained by addition of the IL to the 344 spin-coating precursor solution (Figure 3a).<sup>30,34</sup> The perov- 345 skite film in Figure 3c has large (about 600 nm) crystal 346 domains with uniform and flat surface morphology when 347 grown from the IL-aided MAPbI<sub>3</sub> NPs, in contrast to the 348 pristine CsFAMA (Figure 3b) with smaller (about 400 nm) 349 domains. So, large grains are observed upon the incorporation 350 of MAPbI<sub>3</sub> NPs in the seeded approach. Indeed, the IL has a 351 much higher boiling point than DMF and DMSO solvents, and 352 the interaction between PbI<sub>2</sub> (Lewis acid) and the imidazolium 353

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**Figure 5.** (a) Schematic of the perovskite device via embedded MAPbI<sub>3</sub> NPs in the seeded growth approach. Cross-sectional SEM images of PSC devices fabricated with the (b) MAPbI<sub>3</sub> NP (dark blue circles show voids), (c) pristine CsFAMA, and (d) IL-aided MAPbI<sub>3</sub> NPs/CsFAMA films (red circles show MAPbI<sub>3</sub> NPs embedded in the perovskite film).



**Figure 6.** (a) Reverse scan J-V curves of CsFAMA and MAPbI<sub>3</sub> NPs/CsFAMA PSCs. (b) IPCE spectra of CsFAMA and MAPbI<sub>3</sub> NPs/CsFAMA PSCs. (c) Steady-state stabilized efficiency measured for the CsFAMA and MAPbI<sub>3</sub> NPs/CsFAMA layer-based perovskite solar cells. (d) Dark J-V curves for PSCs without and with MAPbI<sub>3</sub> NPs.

354 IL (Lewis base) slows down the perovskite crystal growth, 355 yielding the large crystal domain perovskite.<sup>45,47</sup> The smoother 356 surface morphology with larger crystal domains reduces grain 357 boundaries, which, in turn, results in charge carrier losses.<sup>48</sup> 358 Improved morphology along with the enhanced cohesion of 359 the brookite TiO<sub>2</sub> NPs/perovskite interface due to the MAPbI<sub>3</sub> 360 NPs may facilitate improved light capture and charge 361 extraction by means of PL quenching and enhanced absorption 362 and quantum efficiency, as shown in Figures 4a, S2a, and 6b, 363 respectively.

To gain insight into the recombination behavior of charge action in the devices, PL emission spectra of the  $FTO-TiO_2/$ 366 MAPbI<sub>3</sub> NP,  $FTO-TiO_2/CsFAMA$ , and  $FTO-TiO_2/$ 

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 $(MAPbI_3 NPs/CsFAMA)$  films were recorded (Figure 4a). 367 PL quenching reveals efficient electron transfer from the 368 perovskite to the ETLs. PL of the FTO $-TiO_2/MAPbI_3 NP$  369 film shows reduced quenching and, thus, less efficient charge 370 transfer. 371

However, the MAPbI<sub>3</sub> NPs/CsFAMA film on FTO-TiO<sub>2</sub> 372 exhibits larger quenching than CsFAMA on FTO-TiO<sub>2</sub> ETL, 373 indicating that carrier recombination is effectively delayed 374 owing to fewer defects and higher crystallinity of the seeded 375 film, as supported by XRD and SEM analyses. We further 376 conducted electrochemical impedance spectroscopy (EIS) to 377 quantify the charge transfer resistance ( $R_{\rm CT}$ ) of the devices. 378 Figure 4b shows Nyquist plots of the MAPbI<sub>3</sub> NP, CsFAMA, 379

perovskite layers		$J_{\rm sc}~({\rm mA/cm^2})$	$V_{\rm oc}~({ m V})$	FF	PCE (%)
MAPbI <sub>3</sub> NPs	champion	15.56	0.91	0.67	9.52
	average $\pm$ SD	$12.9 \pm 1.9$	$0.90 \pm 0.09$	$0.60 \pm 0.09$	$6.9 \pm 1.7$
CsFAMA	champion	23.72	1.06	0.69	17.33
	average $\pm$ SD	$23.3 \pm 0.6$	$1.04 \pm 0.02$	$0.67 \pm 0.02$	$16.3 \pm 0.6$
MAPbI3 NPs/CsFAMA	champion	25.31	1.09	0.70	19.44
	average $\pm$ SD	$24.6 \pm 0.7$	$1.06 \pm 0.02$	$0.70 \pm 0.02$	$18.2 \pm 0.6$

#### Table 1. Outline of the PSC Characteristics<sup>a</sup>

<sup>a</sup>Statistical test (average  $\pm$  standard deviation) was carried on 21, 25, and 33 individual devices with MAPbI<sub>3</sub>, CsFAMA, and MAPbI<sub>3</sub> NPs/CsFAMA, respectively. Champion refers to the highest PCE of the device.

380 and MAPbI<sub>3</sub> NPs/CsFAMA devices at zero bias in the dark. 381 Table S1 shows Nyquist plot fitting analysis parameters. The 382 diameter of the observed semicircles denotes  $R_{CT}$ .<sup>49</sup> The 383 device based on MAPbI<sub>3</sub> NPs exhibits an  $R_{CT}$  value of 3318  $\Omega$ . 384 The CsFAMA device shows a relatively higher  $R_{CT}$  value of 385 141.6  $\Omega$ , whereas  $R_{\rm CT}$  decreases down to 32.84  $\Omega$  with 386 MAPbI<sub>3</sub> NPs embedded in the CsFAMA device. R<sub>CT</sub> reduction 387 improves charge collection efficiency at the interface in the 388 MAPbI<sub>3</sub> NP-seeded film device, as compared to pristine 389 MAPbI<sub>3</sub> NP and CsFAMA-based devices. To explain the 390 influence of IL-assisted MAPbI3 NPs embedded in the 391 CsFAMA film, we carried out time-resolved photolumines-392 cence (TRPL) measurement. Results suggest that the carrier 393 lifetime of the IL-assisted MAPbI3 NPs embedded in the CsFAMA film is roughly twice as long as that in the control 394 395 CsFAMA film (Figure 4c), which indicates that the MAPbI<sub>3</sub> 396 NPs/CsFAMA perovskite film effectively shows reduced 397 nonradiative recombination, thereby prolonging the carrier lifetime (Table S2).<sup>50</sup> 398

Figure 5a shows the complete configuration of a perovskite 399 400 device with MAPbI<sub>3</sub> NPs embedded in the CsFAMA film. It 401 also compares the cross-sectional SEM images of devices with 402 the MAPbI<sub>3</sub> NP (~200 nm thick), CsFAMA (~600-nm thick), 403 and MAPbI<sub>3</sub> NPs/CsFAMA films (~600-nm thick), as shown 404 in Figure 5b-d. We adopted TiO<sub>2</sub> CL/brookite TiO<sub>2</sub> NPs as 405 ETLs on the FTO-glass substrate for efficient charge 406 extraction, improved electron transport, and hole-blocking 407 due to the compact packing.<sup>40</sup> The MAPbI<sub>3</sub> NP-incorporated 408 film device reveals large voids (black circles), which may 409 seriously affect the efficiency and stability of the PSCs. Figure 410 5b shows that a small amount of IL remains within the 411 MAPbI<sub>3</sub> NP film voids that penetrate the MAPbI<sub>3</sub> NP layer, 412 facilitating shunting because of a direct interaction between the 413 Spiro-OMeTAD and TiO<sub>2</sub>/brookite TiO<sub>2</sub> NPs. However, 414 incorporating the CsFAMA into the MAPbI<sub>3</sub> NP wet film 415 greatly improved the coverage of the perovskite film with fewer 416 grain boundaries, minimizing direct contact between Spiro-417 OMeTAD and TiO<sub>2</sub>/brookite TiO<sub>2</sub> NP charge transport 418 materials (Figure 5d). Moreover, the columnar crystal 419 direction, which significantly enhances light capture, reduces 420 recombination and provides effective charge transport, which 421 improves the performance of the PSC.<sup>51</sup>

The current density–voltage (J-V) curves with the two-type 223 configuration of CsFAMA and MAPbI<sub>3</sub> NPs/CsFAMA devices 224 are shown in Figure 6. The forward scan (FS) and reverse scan 225 (RS) J-V curves of the MAPbI<sub>3</sub> NP device are shown in 226 Figure S2b. Their photovoltaic characteristics are summarized 227 in Table 1, comprising  $J_{sc}$ , the open-circuit voltage ( $V_{oc}$ ), the 228 fill factor (FF), and PCE, and a comparison of the FS and RS 229 results is given in Table S3. The best-performing MAPbI<sub>3</sub> NP 230 control device exhibits a  $J_{sc}$  of 15.56 mA/cm<sup>2</sup>, a  $V_{oc}$  of 0.91, an FF of 0.67, and a PCE of 9.52% in the RS direction (Figure 431 S2b). The device with only MAPbI<sub>3</sub> NPs, which exhibits large 432 voids (Figure 5b), shows poor photovoltaic properties. 433

The MAPbI<sub>2</sub> NP-based device configuration leads to strong 434 leakage current and charge carrier recombination owing to 435 smaller NP crystals that retain a large number of grain 436 boundaries (Figure 5b), as inferred by the PL (Figure 4a) and 437 EIS spectra (Figure 4b). This implies that the MAPbI<sub>3</sub> NP film 438 cannot be used as an efficient light absorbing layer. The 439 champion PSC with a conventional CsFAMA absorbing layer 440 exhibits a  $J_{\rm sc}$  of 23.72 mA/cm<sup>2</sup>, a  $V_{\rm oc}$  of 1.06, and an FF of 0.69, 441 yielding a PCE of 17.33% in the RS direction (Figure 6a). The 442 MAPbI<sub>3</sub> NP/CsFAMA device demonstrates a J<sub>sc</sub> of 25.31 mA/ 443 cm<sup>2</sup>, a  $V_{\rm oc}$  of 1.09, and an FF of 0.70, yielding a PCE of 19.44% 444 in the RS direction (Figure 6a). Embedding the MAPbI<sub>3</sub> NPs 445 in the CsFAMA device caused  $J_{sc}$  to increase to 25.31 mA/cm<sup>2</sup>, 446 whereas it was 23.72 mA/cm<sup>2</sup> for the device with a 447 conventional CsFAMA layer. We attribute this enhancement 448 of  $J_{sc}$  to the overall enhancement in the light-harvesting 449 efficiency of the PSCs. Due to the scattering effect of the IL- 450 assisted MAPbI<sub>3</sub> NPs in the MAPbI<sub>3</sub> NP-embedded CsFAMA 451 device, the optical path is increased and more light is absorbed 452 by the perovskite layer.<sup>52</sup> The light scattering effect of MAPbI<sub>3</sub> 453 NPs is expected to be the main factor for the enhancement of 454 light absorption in the devices because the gap was unchanged 455 (Figure S2a). The MAPbI<sub>3</sub> NPs offer promising light 456 manipulation ability to PSCs owing to their size. 53,54 457 Moreover, the MAPbI<sub>3</sub> NPs/CsFAMA device exhibits a 458 significantly lower series resistance  $(R_s)$  of 2.8  $\Omega$  cm<sup>2</sup>, whereas 459 the CsFAMA device has 3.9  $\Omega$  cm<sup>2</sup>, implying that the MAPbI<sub>3</sub> 460 NPs in the CsFAMA device enhanced the carrier extraction (as 461 evident from the PL spectra and EIS spectra), subsequently 462 enhancing  $J_{sc}$ ,  $V_{oc}$ , FF, and PCE. In addition, the higher shunt 463 resistance  $(R_{\rm sh})$  is attributed to the efficient contact with the 464 interfaces. The  $R_{\rm sh}$  values are 1063 and 1546  $\Omega$  cm<sup>2</sup> for the 465 CsFAMA and MAPbI<sub>3</sub> NPs/CsFAMA devices, respectively. 466 The FS and RS J-V curves of the CsFAMA and MAPbI<sub>3</sub> NPs/ 467 CsFAMA film devices are shown in Figure S2c. Hysteresis is 468 present in both J-V characteristics. A significant performance 469 improvement in the MAPbI<sub>3</sub> NPs/CsFAMA PSCs over 470 CsFAMA PSCs is attributed to the larger crystal domains 471 with fewer grain boundaries (i.e., gaps and traps) and high 472 crystallinity, which minimize the recombination of photo- 473 generated carriers.<sup>55</sup> The integrated  $J_{sc}$  values of the IPCE 474 spectra are 22.73 and 23.34 mA/cm<sup>2</sup> for the CsFAMA and 475 MAPbI<sub>3</sub> NPs/CsFAMA devices, respectively (Figure 6b). 476 These values are coherent with the  $J_{sc}$  values extracted from 477 the J-V curves. 478

We carried out the steady-state photocurrent measurement 479 at the maximum power point for the devices with CsFAMA 480 and MAPbI<sub>3</sub> NPs/CsFAMA films. Figure 6c shows the 481



Figure 7. Average (a)  $J_{sc'}$  (b)  $V_{oc'}$  (c) FF, and (d) PCE values of PSCs made with MAPbI<sub>3</sub> NP, CsFAMA, and MAPbI<sub>3</sub> NPs/CsFAMA layers. Error bars express ±1 standard deviation from the average.



**Figure 8.** Water contact angle of the (a) MAPbI<sub>3</sub> NP, (b) CsFAMA, and (c) MAPbI<sub>3</sub> NP-embedded CsFAMA films. (d) Normalized PCE versus time of non-encapsulated MAPbI<sub>3</sub> NPs, CsFAMA, and MAPbI<sub>3</sub> NPs/CsFAMA PSCs after exposure to continuous light illumination (1 sun) for 2.12 h in air with a humidity range of 30-40%. (e) Normalized PCE versus time (in h) of non-encapsulated PSCs stored at ambient with a relative humidity (RH) range of 30-40%.

<sup>482</sup> stabilized efficiency under 1 sun (AM 1.5G) irradiation. The <sup>483</sup> values are 0.83 and 0.92 V for the CsFAMA and MAPbI<sub>3</sub> NPs/ <sup>484</sup> CsFAMA devices, respectively. The MAPbI<sub>3</sub> NPs/CsFAMA-<sup>485</sup> based perovskite device shows a stabilized efficiency of 19% <sup>486</sup> (up to 300 s), which is very close to the efficiency estimated <sup>487</sup> from the J-V measurement in reverse scan (Figure 6a). The <sup>488</sup> stabilized efficiency evidences the impact of larger crystal <sup>489</sup> domains with fewer grain boundaries (i.e., gaps and traps) on <sup>490</sup> the PSC efficiency. Figure 6d shows that the MAPbI<sub>3</sub> NPs/ <sup>491</sup> CsFAMA device possesses a lower dark current density ( $J_{dark}$ ) than the pristine CsFAMA device. A lower dark current density 492 implies a larger  $V_{oc}$ , as observed experimentally. This also 493 indicates that the IL-assisted MAPbI<sub>3</sub> NPs into CsFAMA 494 reduce the leakage current, which is also beneficial to  $J_{sc}$ .<sup>49,56</sup> 495 The IPCE of the device also directly depends on  $J_{dark}$  as IPCE 496 =  $[(J_{light} - J_{dark})hv]/P_{in}e$ .<sup>57</sup> The histogram of PCEs for 497 CsFAMA and MAPbI<sub>3</sub> NPs/CsFAMA devices is shown in 498 Figure S2d. The PCE distribution of the MAPbI<sub>3</sub> NPs/ 499 CsFAMA devices is considerably narrower than that of pristine 500 CsFAMA devices, with a drop in standard deviation from 1.7 501



**Figure 9.** (a) Reverse scan J-V curves of pristine MAPbI<sub>3</sub> and MAPbI<sub>3</sub> NPs/MAPbI<sub>3</sub>-based PSCs. (b) Light-soaking test of pristine MAPbI<sub>3</sub> and MAPbI<sub>3</sub> NPs/MAPbI<sub>3</sub> (non-encapsulated). The resultant devices were measured at 30–40% relative humidity conditions.

502 to 0.6 (absolute PCE). We have also investigated the efficiency 503 of devices grown by the two-step process but without the IL. 504 The PCE of pristine MAPbI<sub>3</sub>/CsFAMA-based PSCs was as 505 high as 17.49% (Figure S3a). Their photovoltaic characteristics 506 are summarized in Table S4. In addition to this, we also 507 investigated the impact of HMImCl (termed as IL) additive on 508 the photovoltaic properties of the CsFAMA perovskite. The IL 509 does not completely dissolve in the CsFAMA precursor s10 solution containing DMF and DMSO mixed solvents. The 511 rather insoluble precursor solution was spin cast on the 512 substrate. The resultant surface morphology was analyzed by 513 SEM (Figure S3b). The SEM image shows insoluble IL 514 contents (white dots) on the surface morphology of the 515 perovskite. The insoluble residual IL in the perovskite film is 516 expected to hamper charge dissociation, transport, and/or 517 recombination, which affects the resulting device performance. 518 PSCs with the CsFAMA/IL film have a  $J_{sc}$  of 21.75 mA/cm<sup>2</sup>, 519  $V_{oc}$  of 1.02 V, FF of 0.52, and PCE of 11.58% in the RS (Figure 520 S3c). Their photovoltaic characteristics are outlined in Table 521 S5. The PCE is much lower than the reference material (with 522 IL-assisted MAPbI<sub>3</sub> NPs embedded CsFAMA), attributed to 523 the insoluble IL contents in the perovskite film.

To confirm the reproducibility of the PSC performance, 21, 525 25, and 33 individual devices based on MAPbI<sub>3</sub> NPs, 526 CsFAMA, and MAPbI<sub>3</sub> NPs/CsFAMA were fabricated, 527 respectively. Their average  $J_{s\sigma}$   $V_{\sigma\sigma}$  FF, and PCE values were 528 compared (Figure 7). Overall, the MAPbI<sub>3</sub> NPs/CsFAMA 529 devices show a larger average PCE of 18.2 ± 0.6% with better 530 reproducibility than the MAPbI<sub>3</sub> NP and CsFAMA devices 531 (6.9 ± 1.7 and 16.3 ± 0.6%, respectively).

Long-term stability is one of the main challenges for market 532 533 adoption of PSCs. Perovskite devices are unstable under moisture, oxygen, light, or heat exposure.<sup>58</sup> Previous reports 534 535 revealed that the defects present at grain boundaries and 536 interfaces are the utmost weakest sites that cause perovskite  $_{537}$  degradation.  $^{59-61}$  In fact, these areas are sensitive to moisture 538 and oxygen, which induce irreversible decomposition of the 539 perovskite.<sup>62</sup> The IL-aided MAPbI<sub>3</sub> NP film retains hydro-540 phobic imidazole rings, which can build a moisture-repelling 541 barricade around the perovskite, thereby improving the device 542 stability. We measured the water contact angle of the 543 perovskite layers at three distinct spots on every film surface. 544 Average values are given in Figure 8. Only the MAPbI<sub>3</sub> NP film 545 in Figure 8a exhibits a higher contact angle of 76.6°, implying 546 the presence of the IL within the MAPbI<sub>3</sub> NP film.<sup>30</sup> The 547 pristine CsFAMA film shows a lower water contact of 54.1°, 548 whereas the IL-assisted MAPbI<sub>3</sub> NPs/CsFAMA film has a

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contact angle of 72.3°, implying the superior hydrophobicity of 549 the MAPbI<sub>3</sub> NP-embedded perovskite film. The contact angle 550 study confirms the cross-sectional SEM images, revealing the 551 MAPbI<sub>3</sub> NPs embedded in the perovskite film with red circles 552 (Figure 5d). Increased hydrophobicity of the MAPbI<sub>3</sub> NPs/ 553 CsFAMA perovskite film is expected to repel moisture and 554 drop water infiltration into the perovskite film under humid 555 conditions. 556

To evaluate further the reliability of the devices, we 557 performed tests under light soaking at ambient atmosphere, 558 as shown in Figure 8d,e. The light-soaking test was performed 559 by continuous exposition of non-encapsulated devices to 1 sun 560 illumination for  $\sim 2$  h in humid air (30–40% RH range). The 561 MAPbI<sub>3</sub> NP device exhibits a noticeable decrease in PCE after 562 a certain period, even though the film has higher hydro- 563 phobicity (Figure 8a). It is attributed to the large voids that 564 function as defect centers/trap states at the interface, which is 565 inconsistent with the cross-sectional SEM image (Figure 5b) 566 and PL (Figure 4a) and EIS results (Figure 4b). Conversely, 567 the MAPbI<sub>3</sub> NPs/CsFAMA and pristine CsFAMA devices 568 retain, respectively, 92 and 83% of their primary efficiency after 569 light soaking (Figure 8d). This stable performance is due to 570 the improved perovskite film quality, limited defect sites, and 571 recombination centers surrounded by the bulk and at the 572 interface (as verified by PL and EIS). We previously reported 573 that highly crystalline, conductive, and large-surface-area 574 brookite TiO<sub>2</sub> NPs facilitate efficient charge transfer kinetics 575 as well as improved device stability compared to only anatase 576 TiO2-based PSCs.<sup>63</sup> We assume that MAPbI3 NPs bridge 577 brookite TiO2 NPs through interparticle necking and scaffold 578 formation, which promotes efficient interfacial charge transfer, 579 improves light capture, and consequently enhances the device 580 performance and stability. Furthermore, we measured the 581 moisture stability of the devices. The J-V curves of the devices 582 were collected (without sealing or encapsulation) before and 583 after the dark storage at ambient atmosphere (RH 30-40%) at 584 25 °C. The normalized PCE versus time (h) is shown in Figure 585 8e. The MAPbI<sub>3</sub> NPs/CsFAMA device does not deteriorate 586 unlike the CsFAMA device. The PCE of the MAPbI3 NPs/ 587 CsFAMA device is stable against moisture, retaining 80% of its 588 original value after 6000 h. In addition, the MAPbI<sub>3</sub> NPs/ 589 CsFAMA device shows no obvious degradation in  $J_{sc}$ ,  $V_{oc}$ , and 590 FF even after 6000 h storage, unlike the CsFAMA device 591 (Figure S4). We notice in Figure S4a-c that for the pristine 592 CsFAMA-based device, performance degradation is mostly 593 caused by a decrease in  $J_{sc}$  and FF, while for the MAPbI<sub>3</sub> NPs/ 594 CsFAMA device, J<sub>sc</sub> and FF decrease marginally. Remarkably, 595

596 both devices almost retain their initial  $V_{\rm oc}$  in the period. We 597 observed that the color of the MAPbI<sub>3</sub> NPs/CsFAMA device 598 became considerably lighter after 6000 h storage, which is 599 mainly due to phase transition,<sup>64</sup> associated with a decrease in 600  $J_{\rm sc}$  (Figure S4a). In addition, phase transition induces changes 601 in the film morphology and the interface, resulting in a 602 decreased FF. Both light-soaking and moisture stability are 603 enhanced in the high-quality perovskite film grown using the 604 MAPbI<sub>3</sub> NP seed-mediated approach.

<sup>605</sup> We further investigated the effectiveness of the incorpo-<sup>606</sup> ration of MAPbI<sub>3</sub> NP seeding for the growth of a MAPbI<sub>3</sub> film, <sup>607</sup> which shows an enhancement of  $J_{sc}$  (Figure 9a) and notable <sup>608</sup> light-soaking stability (Figure 9b). The FS and RS J-V curves <sup>609</sup> and IPCE spectra of the pristine MAPbI<sub>3</sub> and MAPbI<sub>3</sub> NPs/ <sup>610</sup> MAPbI<sub>3</sub> devices are shown in Figure S5a,b.

More importantly,  $J_{sc}$  was improved, retaining a similar trend 611 612 as MAPbI<sub>3</sub> NPs/CsFAMA PSCs. This improvement is 613 provided by the MAPbI<sub>3</sub> seeding NPs embedded in the 614 perovskite for improved light absorption and charge carrier 615 transport and collection. To confirm the reproducibility of the 616 PSC performance, 15 and 24 individual devices based on 617 pristine MAPbI<sub>3</sub> and MAPbI<sub>3</sub> NPs/MAPbI<sub>3</sub> were fabricated, 618 respectively. The average  $I_{sci}$   $V_{oci}$  FF, and PCE values of the 619 PSCs were compared (Figure S5c-f and Table S6). The PSC 620 with the pristine MAPbI<sub>3</sub> film exhibits an average  $J_{sc}$  of 20.96  $\pm$ 621 1.4 mA/cm<sup>2</sup>,  $V_{oc}$  of 1.0  $\pm$  0.03 V, FF of 0.68  $\pm$  0.05, and PCE 622 of 14.20  $\pm$  1.38%. Conversely, the PSC with the MAPbI<sub>3</sub> NPs/ 623 MAPbI<sub>3</sub> film has an average  $J_{sc}$  of 21.89  $\pm$  0.89 mA/cm<sup>2</sup>,  $V_{oc}$  of  $624 \ 1.01 \pm 0.03 \ V$ , FF of 0.71  $\pm$  0.04, and PCE of 15.64  $\pm$  0.36%. 625 The MAPbI<sub>3</sub> NPs/MAPbI<sub>3</sub>-based PSCs yield better reprodu-626 cibility and superior PCE compared to the pristine MAPbI<sub>3</sub>-627 based devices. Furthermore, the FWHM value of the peak 628 decreases from 0.27 for MAPbI<sub>3</sub> to 0.25 for MAPbI<sub>3</sub> NPs/ 629 MAPbI<sub>3</sub> films, implying higher crystallinity of the MAPbI<sub>3</sub> 630 NPs/MAPbI<sub>3</sub> films (Figure S6c). Figure S6f shows the grain 631 size distribution histograms of pristine MAPbI<sub>3</sub> and MAPbI<sub>3</sub> 632 NPs containing the MAPbI<sub>3</sub> film. The MAPbI<sub>3</sub> NPs/MAPbI<sub>3</sub> 633 device presents remarkable light-soaking stability, holding 85% 634 of the initial PCE after 2 h exposure. We attribute these 635 noticeably stabilized light-soaking characteristics to the hydro-636 phobicity (Figure S6b), crystallinity (Figure S6c), and large 637 domains of the IL-aided MAPbI<sub>3</sub> NPs/MAPbI<sub>3</sub> film (Figure 638 S6e) compared to the pristine MAPbI<sub>3</sub> film (Figure S6d).

639 The improved stability of MAPbI<sub>3</sub> NP-seeded growth 640 significantly relies on the following features: first, the more 641 hydrophobic IL-aided MAPbI<sub>3</sub> NPs slow down the CsFAMA 642 growth, forming large crystal domains with fewer grain 643 boundaries (as evident from the XPS and FTIR spectra; 644 Figure 2a–c), which effectively limit the exposure to moisture. 645 Second, the promoted crystals significantly reduce the 646 degradation of the perovskite (Figure 2d). A similar trend 647 occurs in the case of the MAPbI<sub>3</sub> NPs/MAPbI<sub>3</sub> device. 648 Therefore, incorporation of the MAPbI<sub>3</sub> NP seeds into the 649 pristine MAPbI<sub>3</sub> film improves the  $J_{sc}$  and light-soaking 650 stability. These results can serve as a guide to further improve 651 the device stability by choosing a more robust HTM.

# 652 CONCLUSIONS

653 We developed a novel technique based on MAPbI<sub>3</sub> NP seeds 654 embedded in conventional CsFAMA or MAPbI<sub>3</sub> structures, 655 showing that the IL-aided MAPbI<sub>3</sub> NPs significantly promote 656 high-quality perovskite films with large single-crystal domains, 657 improving light harvesting, device performance, and operation 682

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stability. The solar cells based on the MAPbI<sub>3</sub> NPs/CsFAMA 658 configuration exhibit significant enhancement in both device 659 efficiency and stability over time. In addition, significant 660 improvement of  $J_{sc}$  is found in both the MAPbI<sub>3</sub> NPs/ <sub>661</sub> CsFAMA and MAPbI<sub>3</sub> configurations. PSCs using the MAPbI<sub>3</sub> 662 NPs/CsFAMA perovskite exhibit a PCE of 19.44%, which is 663 larger than that of pristine CsFAMA (17.33%). PSCs with 664 MAPbI<sub>3</sub> NPs/CsFAMA still retain 92% of the original PCE 665 value after light-soaking tests with non-encapsulated devices 666 for  $\sim$ 2 h in the air with high (30–40%) humidity. Meanwhile, <sub>667</sub> the PCE of pristine CsFAMA-based PSCs almost decreased to 668 83% of the original value, demonstrating that the MAPbI<sub>3</sub> NP 669 seed-embedded CsFAMA has superior light-soaking stability. 670 Furthermore, the device based on the MAPbI<sub>3</sub> NPs/MAPbI<sub>3 671</sub> structure shows excellent light-soaking stability. The highly 672 hydrophobic IL-aided MAPbI3 NPs/CsFAMA devices are 673 stable against moisture, retaining above 80% of the initial PCE 674 even after 6000 h at ambient (non-encapsulated). Stability is 675 improved in the high-quality perovskite film with large single- 676 crystal domains, which effectively reduce the attack of 677 moisture. The present MAPbI<sub>3</sub> NP-seeded growth demon- 678 strates the possibility to further enhance the efficiency and 679 stability of PSCs by sophisticated defect engineering (e.g., 680 interface recombination and trap passivation). 681

# ASSOCIATED CONTENT

# **Supporting Information**

The Supporting Information is available free of charge at 684 https://pubs.acs.org/doi/10.1021/acsami.1c00677. 685

UV-vis spectra of the perovskite films formed with 686 MAPbI<sub>3</sub> NPs, CsFAMA, and MAPbI<sub>3</sub> NPs/CsFAMA. 687 Forward scan (FS) and reverse scan (RS) J-V curves of 688 the devices with MAPbI<sub>3</sub> NP, CsFAMA, and MAPbI<sub>3</sub> 689 NPs/CsFAMA layers. Histogram of PCEs of PSCs 690 comprising the CsFAMA and MAPbI<sub>3</sub> NPs/CsFAMA 691 layer. Photovoltaic variables of PSCs fabricated with 692 CsFAMA and MAPbI<sub>3</sub> NPs containing CsFAMA film: 693  $J_{sct}$   $V_{oct}$  and FF, as a functions of storage periods (h). FS 694 and RS J-V features of the devices with pristine MAPbI<sub>3</sub> 695 and MAPbI<sub>3</sub> NPs embedded MAPbI<sub>3</sub> film and IPCE 696 spectra of devices with a pristine MAPbI<sub>3</sub> and MAPbI<sub>3</sub> 697 NPs embedded MAPbI<sub>3</sub> film. Average  $J_{sc}$ ,  $V_{oc}$ , FF, and 698 PCE values of PSCs fabricated with MAPbI<sub>3</sub> NPs, 699 CsFAMA, and MAPbI<sub>3</sub> NPs/CsFAMA layers. Water 700 contact angle measurements of pristine MAPbI<sub>3</sub> film and 701 MAPbI<sub>3</sub> NPs embedded MAPbI<sub>3</sub> film. XRD spectra of 702 pristine MAPbI<sub>3</sub> and MAPbI<sub>3</sub> NPs seeding embedded 703 MAPbI<sub>3</sub> film. SEM images of pristine MAPbI<sub>3</sub> and 704 MAPbI<sub>3</sub> NPs/MAPbI<sub>3</sub> film. The grain size distribution 705 histograms of pristine MAPbI3 and MAPbI3 NPs 706 containing the MAPbI<sub>3</sub> film. Nyquist plots fitting 707 analysis parameters. TRPL spectra of CsFAMA and 708 MAPbI<sub>3</sub> NPs/CsFAMA-based perovskite films. Outline 709 of device performance features with MAPbI<sub>3</sub> NPs, 710 CsFAMA, and MAPbI<sub>3</sub> NPs/CsFAMA-based photo- 711 sensitive perovskite layers. Summary of device perform- 712 ance characteristics with pristine MAPbI3 and MAPbI3 713 NPs/MAPbI<sub>3</sub> layers (PDF) 714

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### 715 **AUTHOR INFORMATION**

#### 716 Corresponding Authors

- Md. Shahiduzzaman Nanomaterials Research Institute, 717
- Kanazawa University, Kakuma, Kanazawa 920-1192, 718
- Japan; orcid.org/0000-0002-3092-7793; Phone: +81-719
- 76-234-4937; Email: shahiduzzaman@se.kanazawa-u.ac.jp 720
- Jean-Michel Nunzi Nanomaterials Research Institute, 721
- Kanazawa University, Kakuma, Kanazawa 920-1192, 722
- Japan; Department of Physics, Engineering Physics and 723
- 724 Astronomy, Queens University, Kingston, Ontario K7L 3N6,
- 725 *Canada*; orcid.org/0000-0001-5490-4273;
- Email: nunzijm@queensu.ca 726
- Tetsuya Taima Nanomaterials Research Institute, 727
- Kanazawa University, Kakuma, Kanazawa 920-1192, 728
- Japan; Graduate School of Frontier Science Initiative and 729
- Graduate School of Natural Science and Technology, 730
- Kanazawa University, Kakuma, Kanazawa 920-1192, 731
- Japan; Email: taima@se.kanazawa-u.ac.jp 732

#### 733 Authors

- LiangLe Wang Graduate School of Frontier Science 734
- Initiative, Kanazawa University, Kakuma, Kanazawa 920-735 1192, Japan 736
- Shoko Fukaya Graduate School of Frontier Science 737
- 738 Initiative, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan 739
- Ersan Y. Muslih Graduate School of Natural Science and 740 Technology, Kanazawa University, Kakuma, Kanazawa 920-741 1192, Japan; orcid.org/0000-0002-2972-6214 742

Atsushi Kogo - National Institute of Advanced Industrial 743 Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, 744 Japan; orcid.org/0000-0002-9837-5585 745

Masahiro Nakano - Graduate School of Natural Science and 746 Technology, Kanazawa University, Kakuma, Kanazawa 920-747

- 1192, Japan; orcid.org/0000-0002-9231-4124 748
- Makoto Karakawa Nanomaterials Research Institute, 749
- Kanazawa University, Kakuma, Kanazawa 920-1192, 750
- Japan; Graduate School of Frontier Science Initiative and 751
- Graduate School of Natural Science and Technology, 752
- Kanazawa University, Kakuma, Kanazawa 920-1192, 753
- Japan; orcid.org/0000-0001-7412-8179 754 Kohshin Takahashi – Graduate School of Natural Science 755

and Technology, Kanazawa University, Kakuma, Kanazawa 756

- 920-1192, Japan 757 Koji Tomita – Department of Chemistry, School of Science, 758
- Tokai University, Hiratsuka, Kanagawa 259-1292, Japan 759 Tsutomu Miyasaka – Graduate School of Engineering, Toin 760
- University of Yokohama, Kuroganecho, Yokohama 225-8503, 761 Japan; orcid.org/0000-0001-8535-7911
- 762

763 Complete contact information is available at: 764 https://pubs.acs.org/10.1021/acsami.1c00677

# 765 Author Contributions

766 <sup>O</sup>M.S. and L.W. contributed equally to this work.

#### 767 Notes

768 The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS 769

770 This study was financially supported by the Grant-in-Aid for 771 Scientific Research (Grant Number 20H02838). This study 772 was partially supported by 2019 Research Grant from the 773 Mitani Foundation for Research and Development. The authors thank Dr. Md. Akhtaruzzaman (The National 774 University of Malaysia, Malaysia) for valuable discussions. 775

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