Organometal halide perovskite solar cells (PSCs) are presently the epitome of energy harvesting in photovoltaic materials.1−7 Intensive research efforts all over the world have started in 2009 after Miyasaka.8 The power conversion efficiencies (PCEs) of PSCs (25.5%) in 2020 have approached or exceeded those of other photovoltaic materials, such as silicon (26.7%), copper indium gallium selenide solar cells (22.9%), and cadmium telluride (22.1%).9 However, improvement of the operational stability is necessary for PSC commercialization.10−12 Both extrinsic (environmental) and intrinsic factors affect the PSC stability. Environmental factors such as moisture, oxygen, and light or heat can damage the photoactivity of PSCs.13,14 The intrinsic stability of the perovskite structure is affected by defects, both in the perovskite film and at the interface between the perovskite and charge transport layers.15 Limited perovskite stability originates from the hygroscopic nature of organic cations, under-coordinated lead atoms, as well as ion migration and thermal degradation. The hygroscopic character can be remediated by encapsulation,16 and thermal stability can be improved by engineering the perovskite composition and inorganic hole-transport materials (HTMs).17−21 Ion migration in perovskite layers is an additional cause of PSC degradation. Ion transport initiated by the electric field induced by illumination can be reduced or even suppressed by grain-boundary passivation through interface engineering.22−24 However, to realize the full potential of PSCs, simultaneous improvement in device engineering needs to be considered.22 Various materials have been added to the perovskite film, such as polymers,25−27 fullerences,25 metal halide salts,26−28 organic halide salts,29 nanoparticles,30−31 and ionic liquids (ILs),32−34 leading to highly efficient and stable PSCs. Among these materials, ILs also known as green solvents have prompted significant consideration as an additive, a solvent, an interface modifier, and an independent electron transport layer (ETL) for fabricating efficient and stable PSCs because of their high thermal and electrochemical robustness, low-vapor pressure, and high ionic conductivity.32 Previously, we reported imidazole-based IL in a MAPbI3 precursor solution containing 33 ion liquid-assisted MAPbI3 nanoparticle-seeded growth, dense perovskite, perovskite solar cells, stability
only N,N-dimethylformamide (DMF) as a solvent and found that uniform spherical MAPbI3 nanoparticles (NPs) formed after spin-coating. ILs allow rapid crystallization and formation of uniform MAPbI3 NPs. The resulting MAPbI3 NPs were used solely as a perovskite photoactive layer in PSCs.10–13,31,34 Seo et al.13,35 fabricated a highly crystalline and uniform perovskite film with large crystal domains by depositing methylammonium formate as an IL to the precursor, resulting in champion planar PSCs with a stabilized power output of 19.5%. Wang et al.36 reported water-soluble triazolium IL-induced perovskite, improving the stability and efficiency of PSCs, maintaining an initial efficiency of around 80% for 3500 h under relative humidity and thermal conditions. Recently, Bai and colleagues reported the use of IL in a triple-cation perovskite precursor solution, increasing the efficiency and long-term stability of the device,8 which remained stable for more than 1800 h under continuous simulated sunlight exposure.

Over the last few years, the use of seeding growth offered an attractive approach to aid the growth of high-quality perovskite films, improving the PSC stability while maintaining its efficiency. Li et al.37 demonstrated an intermixing-seeded growth technique for enhancing the device performance of PSCs by adding a small amount of PbS NPs as the seed during film formation. The authors stated that PbS NPs were capped with methylammonium iodide precursor through interfacial engineering with ligand exchange, which could function as effective heterogeneous nucleation sites to promote the perovskite lattice formation, consequently providing high-performance PSCs. Recently, Zhao et al.38 reported a similar concept of seeding growth approach that was applied to modulate the perovskite crystallization by adding perovskite seed crystals into a PbI2 film. A perovskite seeding growth approach was used to fabricate highly stable Cs-containing FAPbI3-based PSCs, which retained over 60% of their initial efficiency after 140 h at maximum power point under one sun illumination. Zhang et al.39 also produced a self-seeding growth of high-performance PSCs with a PCE of 20.30%, retaining 80% of the original PCE over 4680 h storage at the ambient. This self-seeding growth can be implemented by repeated coating of a similar perovskite precursor solution. These studies suggest that the beneficial effect of the seeding growth approach facilitates fabrication of higher-quality perovskite films, subsequently improving the efficiency and stability of the resultant PSCs. As far as we know, despite significant progress in the improvement of performance in the seeding growth-based PSCs, the use of IL-aided perovskite NP seeding growth in the fabrication of higher-quality perovskite films with remarkable PSC efficiency and stability has not been explored yet.

In this study, we designed a novel technique in which the pristine Cs0.05(FA0.83MA0.17)0.95Pb(I0.83Br0.17)3 (termed as CsFAMA) or pristine MAPbI3 perovskite is grown by IL-assisted MAPbI3 NP seeds to fabricate higher-quality perovskite films with large crystal domains, subsequently improving the efficiency and stability of the devices. Notably, the short-circuit density (Jsc) improved in the CsFAMA or MAPbI3 devices embedded with NPs using the MAPbI3 NP seeding approach. To produce dense perovskite films, we dropped a neat CsFAMA precursor solution on a wet film of the as-deposited IL-assisted MAPbI3 NP clusters. The perovskite nuclei with fewer seed clusters regrow during crystallization, leading to the improvement in structural and optoelectronic properties. We show that the use of a flat and dense perovskite film with high crystallinity and large domain size leads to more efficient charge carrier collection and thus better photovoltaic performances. In addition, this strategy enables a significant improvement in operational stability. Encouragingly, a highly hydrophobic perovskite surface was achieved using the IL-assisted MAPbI3 NPs embedded in the CsFAMA film, which significantly improved the light-soaking and moisture stability. Interestingly, also in the moisture stability, IL-aided MAPbI3 NPs/CsFAMA-based devices retained around 80% of the initial characteristics after 6000 h storage at ambient under 30–40% humidity. More importantly, a similar trend with the MAPbI3 NPs/MAPbI3 structure-based PSCs was observed for the light-soaking stability.

### EXPERIMENTAL METHODS

**Materials.** Fluorine-doped tin oxide (FTO)-coated glass was purchased from Asahi Glass (Tokyo, Japan). 1-Hexyl-3-methylimidida-zolium chloride (HMImCl, 97% purity), chlorobenzene (CB), 150 zirconium chloride (ZrCl4) (97% purity), chlorobenzene (CB), 150 titanium di-isopropoxide bis-(acetylacetonate) Ti(acac)2(OiPr)2, 150 and isopropanol (IPA) were purchased from Sigma-Aldrich (St. Louis, MO). 2-Propanol (99.9% purity) was purchased from Wako Pure Chemical (Tokyo, Japan). Methylammonium bromide (MABr), methylammonium iodide (MAI), formamidinium iodide (FAI), cesium iodide (CsI), lead bromide (105), and lead iodide (105) precursors were purchased from TCI (Tokyo, Japan). N,N- Dimethylformamide (DMF, 99.5% purity) and dimethyl sulfoxide (DMSO, 99.5% purity) were purchased from Wako Pure Chemical (Tokyo, Japan). Spiro-OMeTAD (99.8% purity) was purchased from Lumtec (New Taipei City, Taiwan).

**Device Fabrication.** A patterned FTO-glass substrate was sequentially cleaned by sonication with a commercial detergent in water, deionized water, acetone, and IPA for 15 min. The cleaned FTO substrate was then nitrogen-dried and oxygen-plasma-treated for 20 min prior to use. A 40 nm thick TiO2 compact layer (CL) was prepared on the FTO-glass substrate as follows. The TiO2 CL was spin-coated from 0.15 M Ti(acac)4(OiPr)2 in 2-propanol at 2000 rpm for 30 s, and the substrate was dried on a hot plate at 120 °C for 5 min. Two additional coatings with higher Ti(acac)4(OiPr)2 solution concentration (0.3 M) were performed at the same spinning conditions (2000 rpm, 30 s) and dried at 120 °C for 5 min. The substrate was further treated in a muffle furnace at 450 °C for 30 min. The single-crystal brookite TiO2 NPs were synthesized at pH 10 by hydrothermal synthesis, as reported in our previous study. The brookite TiO2 NP colloidal suspension was spin-coated at 2000 rpm for 30 s on the TiO2 CL and annealed for 5 min at 100 °C, followed by three coating cycles (optimum condition), and finally baked at 180 °C for 60 min in a hot plate. The MAPbI3 perovskite NP films were prepared following our previous report. The triple-cation-based perovskor precursor solution with 5% Cs was prepared by mixing with FA/MA in the DMF and DMSO (4:1) solvent mixture. The perovskite film was then dried in an infrared lamp. The perovskite film was deposited with a chemical formula of Cs0.05(FA0.83MA0.17)0.95Pb(I0.83Br0.17)3, where the Cs fraction is x = 0.05 (Cs 5%), which was fabricated. The stock solution of FAI (1 M), PbI2 (1.1 M), MABr (0.2 M), and PbBr2 (0.2 M) was mixed in anhydrous DMF/DMSO (4:1), and an appropriate volume of CsI solution was added from the CsI stock solution (1.8 M) in DMSO to achieve 5% Cs solution. Prior to spin-coating, the mixed precursor solution was stirred at 70 °C for 60 min. The mixed perovskite solution was spin-coated in the following steps: first at 0 rpm for 10 s, second at 1000 rpm for 10 s, and third at 6000 rpm for 20 s. In the second step, 500 μL of CB solvent was dripped 5 s before the spin-coating starts. The samples were readily transferred to a hot plate at 100 °C for 60 min. In addition, the pristine MAPbI3 precursor solution was prepared as described in our previous report. A precursor solution was prepared by dissolving spiro-OMeTAD, lithium salt (9.1 mg), cobalt (8.7 mg), and 4-tet-butylpyridine 190 (28.8 μL) in 1000 μL of chlorobenzene under stirring at 800 rpm for 1 min for 6 h and used as the hole-transport layer (HTL). The as-
The incident photon-to-electron conversion efficiency (IPCE) spectra were recorded using a monochromatic xenon arc light system (Bunkoukeiki, SMI-250JA).

**RESULTS AND DISCUSSION**

The fabrication of MAPbI₃ NP-based perovskite films with embedded IL-aided MAPbI₃ NPs is schematized in Figure 1. The inset shows the chemical structure of HMImCl (termed as IL), the AFM images of MAPbI₃ small clusters and MAPbI₃ 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.
configuration of CsFAMA, there are several potential binding configurations between the IL and the perovskite. XPS data show the interaction between the IL and the perovskite involving methylimidazolium and hexyl chain as a head and tail in 1-hexyl-3-methylimidazolium, respectively. As evident from XPS, the chloride with a negative charge in the IL tends to bind to the Pb\(^{2+}\) at the perovskite crystal. In addition, the amino group with a lone electron pair in IL forms Pb\(^{-}\)N\(_{f}\) bonds at the perovskite crystal. As shown in Figure 2a, the Pb 4f spectrum of the CsFAMA perovskite film exhibits two characteristic peaks at 138.5 and 143.3 eV, corresponding to the spin-orbit splitting of the Pb 4f\(_{7/2}\) and 4f\(_{5/2}\) constituents, respectively. The resultant signals move to lower binding energies of 138.3 and 143.1 eV, respectively, while using IL-assisted MAPbI\(_3\) NPs as seeds embedded in the CsFAMA structure, which confirms the coordination interaction between the imidazolium ring and Pb\(^{2+}\) defects. Moreover, the I 3d spectra shift upon the use of IL-assisted MAPbI\(_3\) NPs from 619.3 to 618.2 eV (Figure 2b), suggesting an interaction between the imidazolium and PbI\(_3\) defects and a reduced interaction between \(\Gamma\) and strongly electronegative Pb\(^{2+}\). The presence of the IL also appears in the FTIR spectrum (Figure 2c). The FTIR peaks at 3700–3000 cm\(^{-1}\) indicate the free N–H bond from the IL that has a higher vibration energy than the N–H bond in methylammonium that is trapped in the perovskite structure. In addition, N–H peaks from the IL-assisted sample are broadened, whereas N–H peaks from non-IL sample are sharper. The broad peak at 3700–3000 cm\(^{-1}\) indicates N–H bonding in methylimidazolium, which under- goes hydrogen bonding with halogens on the perovskite surface, and these halogens are more likely to make a coordination bonding with lead or with methylammonium, formamidinium, and cesium that might have ended up on the perovskite surface. Even, lead can end up at the surface due to crystal defects. These elements are more likely positive active sites for the IL. Thus, chloride as the negative charge of the IL can bind with these positive sites. It finally ensures that the IL is attached on the perovskite when the perovskite crystal has formed completely. It can be concluded that the IL surrounds the perovskite with head attached to the perovskite surface, meanwhile the IL tail keeps off from the perovskite (Figure 1). The resulting hydrophobicity may improve the IL-assisted MAPbI\(_3\) NP-embedded CsFAMA film, thus, increasing the stability of the devices.

The XRD patterns of the MAPbI\(_3\) NP, CsFAMA, and MAPbI\(_3\) NPs/CsFAMA films are shown in Figure 2d. The peaks at 20.02, 24.52, and 26.57\(^{\circ}\) significantly reduced and shifted because some chloride could exchange with iodine in

![Figure 2. XPS spectra of the perovskite films formed with the CsFAMA and MAPbI\(_3\) NPs/CsFAMA films: (a) Pb 4f and (b) I 3d. (c) FTIR spectra of the perovskite films formed with and without the MAPbI\(_3\) NP film. (d) XRD spectra of the perovskite films formed with MAPbI\(_3\) NPs, CsFAMA, and MAPbI\(_3\) NPs/CsFAMA.](image-url)
the perovskite structure. Although it still reveals the perovskite structure, the substitution can change the d-spacing. The diffraction peaks at 2\(\theta\) angles of 14.1 and 28.4° in the MAPbI\(_3\) NP, CsFAMA, and MAPbI\(_3\) NPs/CsFAMA films correspond to the (110) and (220) crystal planes. The absence of the PbI\(_2\) peak at 12.6° in all cases suggests the complete consumption of PbI\(_2\). The full width at half-maximum (FWHM) of the (110) diffraction peak is narrowed because of the incorporation of MAPbI\(_3\) NPs with the CsFAMA perovskite, indicative of the larger perovskite crystal domains also visible in the SEM images (Figure 3c). The FWHM of the peak decreases from 0.26 (CsFAMA) to 0.24 (MAPbI\(_3\) NPs/CsFAMA) with incorporation of the NP seeds. Lower FWHM also gives evidence of the higher crystallinity of the MAPbI\(_3\) NPs/CsFAMA films. Light absorption is slightly higher for the MAPbI\(_3\) NP-embedded CsFAMA film (Figure S2a). More importantly, the overlapping spectra in the longer wavelength area (near 770 nm) show that the band gap is unchanged.

Figure 3a–c shows SEM images taken from the top of the MAPbI\(_3\) NP, CsFAMA, and MAPbI\(_3\) NPs/CsFAMA films. Smooth morphology and crystallinity of the perovskite films enable efficient device performance and stability. The histograms of grain size distribution, along with Gaussian fittings, are given in Figure 3d–f. The average grain sizes of MAPbI\(_3\) NP, CsFAMA, and MAPbI\(_3\) NPs/CsFAMA films are 156, 380, and 572 nm, respectively. MAPbI\(_3\) NPs with spherical shape were obtained by addition of the IL to the spin-coating precursor solution (Figure 3a).30,34 The perovskite film in Figure 3c has large (about 600 nm) crystal domains with uniform and flat surface morphology when grown from the IL-aided MAPbI\(_3\) NPs, in contrast to the pristine CsFAMA (Figure 3b) with smaller (about 400 nm) domains. So, large grains are observed upon the incorporation of MAPbI\(_3\) NPs in the seeded approach. Indeed, the IL has a much higher boiling point than DMF and DMSO solvents, and the interaction between PbI\(_2\) (Lewis acid) and the imidazolium...
IL (Lewis base) slows down the perovskite crystal growth, yielding the large crystal domain perovskite. The smoother surface morphology with larger crystal domains reduces grain boundaries, which, in turn, results in charge carrier losses. Improved morphology along with the enhanced cohesion of the brookite TiO2 NPs/perovskite interface due to the MAPbI3 NPs may facilitate improved light capture and charge extraction by means of PL quenching and enhanced absorption and quantum efficiency, as shown in Figures 4a, S2a, and 6b, respectively.

To gain insight into the recombination behavior of charge carriers in the devices, PL emission spectra of the FTO–TiO2/MAPbI3 NP, FTO–TiO2/CsFAMA, and FTO–TiO2/(MAPbI3 NPs/CsFAMA) films were recorded (Figure 4a). PL quenching reveals efficient electron transfer from the perovskite to the ETLs. PL of the FTO–TiO2/MAPbI3 NP film shows reduced quenching and, thus, less efficient charge transfer.

However, the MAPbI3 NPs/CsFAMA film on FTO–TiO2 exhibits larger quenching than CsFAMA on FTO–TiO2 ETL, indicating that carrier recombination is effectively delayed owing to fewer defects and higher crystallinity of the seeded film, as supported by XRD and SEM analyses. We further conducted electrochemical impedance spectroscopy (EIS) to quantify the charge transfer resistance (Rct) of the devices. Figure 4b shows Nyquist plots of the MAPbI3 NP, CsFAMA, and MAPbI3 NPs/CsFAMA.
and MAPbI₃ NPs/CsFAMA devices at zero bias in the dark. Table S1 shows Nyquist plot fitting analysis parameters. The diameter of the observed semicircles denotes $R_{CT}$. The device based on MAPbI₃ NPs exhibits an $R_{CT}$ value of 3318 Ω. The CsFAMA device shows a relatively higher $R_{CT}$ value of 141.6 Ω, whereas $R_{CT}$ decreases down to 32.84 Ω with MAPbI₃ NPs embedded in the CsFAMA device. $R_{CT}$ reduction improves charge collection efficiency at the interface in the MAPbI₃ NP-seeded film device, as compared to pristine MAPbI₃ NP and CsFAMA-based devices. To explain the influence of IL-assisted MAPbI₃ NPs embedded in the CsFAMA film, we carried out time-resolved photoluminescence (TRPL) measurement. Results suggest that the carrier lifetime of the IL-assisted MAPbI₃ NPs embedded in the CsFAMA film is roughly twice as long as that in the control CsFAMA film (Figure 4c), which indicates that the MAPbI₃ NPs/CsFAMA perovskite film effectively shows reduced nonradiative recombination, thereby prolonging the carrier lifetime (Table S2). Figure 5a shows the complete configuration of a perovskite device with MAPbI₃ NPs embedded in the CsFAMA film. It also compares the cross-sectional SEM images of devices with the MAPbI₃ NP (~200 nm thick), CsFAMA (~600-nm thick), and MAPbI₃ NPs/CsFAMA films (~600-nm thick), as shown in Figure S2 b–d. We adopted TiO₂/CL/brookite TiO₂ NPs as ETLs on the FTO-glass substrate for efficient charge extraction, improved electron transport, and hole-blocking due to the compact packing. The MAPbI₃ NP-incorporated film device reveals large voids (black circles), which may seriously affect the efficiency and stability of the PSCs. Figure 5b shows that a small amount of IL remains within the MAPbI₃ NP film voids that penetrate the MAPbI₃ NP layer, facilitating shunting because of a direct interaction between the Spiro-OMeTAD and TiO₂/brookite TiO₂ NPs. However, incorporating the CsFAMA into the MAPbI₃ NP wet film greatly improved the coverage of the perovskite film with fewer grain boundaries, minimizing direct contact between Spiro-OMeTAD and TiO₂/brookite TiO₂ NP charge transport materials (Figure 5d). Moreover, the columnar crystal direction, which significantly enhances light capture, reduces recombination and provides effective charge transport, which improves the performance of the PSC. The current density–voltage ($J–V$) curves with the two-type configuration of CsFAMA and MAPbI₃ NPs/CsFAMA devices are shown in Figure 6. The forward scan (FS) and reverse scan (RS) $J–V$ curves of the MAPbI₃ NP device are shown in Figure S2b. Their photovoltaic characteristics are summarized in Table 1, comprising $J_{sc}$ the open-circuit voltage ($V_{oc}$), the fill factor (FF), and PCE, and a comparison of the FS and RS results is given in Table S3. The best-performing MAPbI₃ NP control device exhibits a $J_{sc}$ of 15.56 mA/cm², a $V_{oc}$ of 0.91, an FF of 0.67, and a PCE of 9.52% in the RS direction (Figure S2b). The device with only MAPbI₃ NPs, which exhibits large voids (Figure S5b), shows poor photovoltaic properties. The MAPbI₃ NP-based device configuration leads to strong leakage current and charge carrier recombination owing to smaller NP crystals that retain a large number of grain boundaries (Figure 5b), as inferred by the PL (Figure 4a) and EIS spectra (Figure 4b). This implies that the MAPbI₃ NP film cannot be used as an efficient light absorbing layer. The champion PSC with a conventional CsFAMA absorbing layer exhibits a $J_{sc}$ of 23.72 mA/cm², a $V_{oc}$ of 1.06, and an FF of 0.69, yielding a PCE of 17.33% in the RS direction (Figure 6a). The MAPbI₃ NP/CsFAMA device demonstrates a $J_{sc}$ of 25.31 mA/cm², a $V_{oc}$ of 1.09, and an FF of 0.70, yielding a PCE of 19.44% in the RS direction (Figure 6a). Embedding the MAPbI₃ NPs in the CsFAMA device caused $J_{sc}$ to increase to 25.31 mA/cm², whereas it was 23.72 mA/cm² for the device with a conventional CsFAMA layer. We attribute this enhancement of $J_{sc}$ to the overall enhancement in the light-harvesting efficiency of the PSCs. Due to the scattering effect of the IL-assisted MAPbI₃ NPs in the MAPbI₃ NP-embedded CsFAMA device, the optical path is increased and more light is absorbed by the perovskite layer. The light scattering effect of MAPbI₃ NPs is expected to be the main factor for the enhancement of light absorption in the devices because the gap was unchanged. The MAPbI₃ NPs offer promising light manipulation ability to PSCs owing to their size. Moreover, the MAPbI₃ NPs/CsFAMA device exhibits a significantly lower series resistance ($R_S$) of 2.8 Ω cm², whereas the CsFAMA device has 3.9 Ω cm², implying that the MAPbI₃ NPs in the CsFAMA device enhanced the carrier extraction (as evident from the PL spectra and EIS spectra), subsequently enhancing $J_{sc}$, $V_{oc}$, FF, and PCE. In addition, the higher shunt resistance ($R_q$) is attributed to the efficient contact with the interfaces. The $R_s$ values are 1063 and 1546 Ω cm² for the CsFAMA and MAPbI₃ NPs/CsFAMA devices, respectively. The FS and RS $J–V$ curves of the CsFAMA and MAPbI₃ NPs/CsFAMA film devices are shown in Figure S2c. Hysteresis is present in both J–V characteristics. A significant performance improvement in the MAPbI₃ NPs/CsFAMA PSCs over CsFAMA PSCs is attributed to the larger crystal domains with fewer grain boundaries (i.e., gaps and traps) and high crystallinity, which minimize the recombination of photo-generated carriers. The integrated $J_{sc}$ values of the IPCE spectra are 22.73 and 23.34 mA/cm² for the CsFAMA and MAPbI₃ NPs/CsFAMA devices, respectively (Figure 6b). These values are coherent with the $J_{sc}$ values extracted from the $J–V$ curves.

We carried out the steady-state photocurrent measurement at the maximum power point for the devices with CsFAMA and MAPbI₃ NPs/CsFAMA films. Figure 6c shows the

<table>
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<th>perovskite layers</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
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<td>1.06 ± 0.02</td>
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"Statistical test (average ± standard deviation) was carried on 21, 25, and 33 individual devices with MAPbI₃, CsFAMA, and MAPbI₃ NPs/CsFAMA, respectively. Champion refers to the highest PCE of the device."
482 stabilized efficiency under 1 sun (AM 1.5G) irradiation. The values are 0.83 and 0.92 V for the CsFAMA and MAPbI3 NPs/CsFAMA devices, respectively. The MAPbI3 NPs/CsFAMA-based perovskite device shows a stabilized efficiency of 19\% (up to 300 s), which is very close to the efficiency estimated from the J–V measurement in reverse scan (Figure 6a). The stabilized efficiency evidences the impact of larger crystal domains with fewer grain boundaries (i.e., gaps and traps) on the PSC efficiency. Figure 6d shows that the MAPbI3 NPs/CsFAMA device possesses a lower dark current density (J\text{dark}) than the pristine CsFAMA device. A lower dark current density implies a larger V\text{oc} as observed experimentally. This also indicates that the IL-assisted MAPbI3 NPs into CsFAMA reduce the leakage current, which is also beneficial to J\text{sc}. The IPCE of the device also directly depends on J\text{dark} as IPCE = [(J\text{light} – J\text{dark})hv]/P\text{inc}. The histogram of PCEs for CsFAMA and MAPbI3 NPs/CsFAMA devices is shown in Figure S2d. The PCE distribution of the MAPbI3 NPs/CsFAMA devices is considerably narrower than that of pristine CsFAMA devices, with a drop in standard deviation from 1.7 to 1.3.

Figure 7. Average (a) J\text{sc}, (b) V\text{oc}, (c) FF, and (d) PCE values of PSCs made with MAPbI3 NP, CsFAMA, and MAPbI3 NPs/CsFAMA layers. Error bars express ±1 standard deviation from the average.

Figure 8. Water contact angle of the (a) MAPbI3 NP, (b) CsFAMA, and (c) MAPbI3 NP-embedded CsFAMA films. (d) Normalized PCE versus time of non-encapsulated MAPbI3 NPs, CsFAMA, and MAPbI3 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%.
The PCE of pristine MAPbI3/CsFAMA-based PSCs was as high as 17.49% (Figure S3a). Their photovoltaic characteristics are summarized in Table S4. In addition to this, we also investigated the impact of HMImCl (termed as IL) additive on the photovoltaic properties of the CsFAMA perovskite. The IL does not completely dissolve in the CsFAMA precursor solution containing DMF and DMSO mixed solvents. The rather insoluble precursor solution was spin cast on the substrate. The resultant surface morphology was analyzed by SEM (Figure S3b). The SEM image shows insoluble IL contents (white dots) on the surface morphology of the perovskite. The insoluble residual IL in the perovskite film is expected to hamper charge dissociation, transport, and/or recombination, which affects the resulting device performance.

Perovskite TiO2 NPs facilitate efficient charge transfer kinetics and as well as improved device stability compared to only anatase TiO2-based PSCs.63 We assume that MAPbI3 NPs bridge brookite TiO2 NPs through interparticle necking and scaffold formation, which promotes efficient interfacial charge transfer, improves light capture, and consequently enhances the device performance and stability. Furthermore, we measured the moisture stability of the devices. The J−V curves of the devices were collected (without sealing or encapsulation) before and after the dark storage at ambient atmosphere (RH 30−40%) at 25 °C for 25 days. Increased hydrophobicity of the MAPbI3 NPs/MAPbI3-based PSCs (Figure 8a). The MAPbI3 NPs/MAPbI3-based PSCs exhibit a noticeably higher contact angle of 76.6°, implying the superior hydrophobicity of the MAPbI3 NPs embedded perovskite film. The contact angle study confirms the cross-sectional SEM images, revealing the MAPbI3 NPs embedded in the perovskite film with red circles (Figure 8d). Increased hydrophobicity of the MAPbI3 NPs/CsFAMA perovskite film is expected to repel moisture and drop water infiltration into the perovskite film under humid conditions.

To evaluate further the reliability of the devices, we performed tests under light soaking at ambient atmosphere, as shown in Figure 8e. The light-soaking test was performed by continuous exposure of non-encapsulated devices to 1 sun illumination for ~2 h in humid air (30−40% RH range). The MAPbI3 NP device exhibits a noticeable decrease in PCE after a certain period, even though the film has higher hydrophobicity (Figure 8a). It is attributed to the large voids that function as defect centers/trap states at the interface, which is inconsistent with the cross-sectional SEM image (Figure 3b) and PL (Figure 4a) and EIS results (Figure 4b). Conversely, the MAPbI3 NPs/CsFAMA and pristine CsFAMA devices retain, respectively, 92 and 83% of their primary efficiency after light soaking (Figure 8d). This stable performance is due to the improved perovskite film quality, limited defect sites, and recombination centers surrounded by the bulk and at the interface (as verified by PL and EIS). We previously reported that highly crystalline, conductive, and large-surface-area brookite TiO2 NPs facilitate efficient charge transfer kinetics as well as improved device stability compared to only anatase TiO2-based PSCs.63 We assume that MAPbI3 NPs bridge brookite TiO2 NPs through interparticle necking and scaffold formation, which promotes efficient interfacial charge transfer, improves light capture, and consequently enhances the device performance and stability. Furthermore, we measured the moisture stability of the devices. The J−V curves of the devices were collected (without sealing or encapsulation) before and after the dark storage at ambient atmosphere (RH 30−40%) at 25 °C. The normalized PCE versus time (h) is shown in Figure 8e. The MAPbI3 NPs/CsFAMA device does not deteriorate unlike the CsFAMA device. The PCE of the MAPbI3 NPs/CsFAMA device is stable against moisture, retaining 80% of its original value after 6000 h. In addition, the MAPbI3 NPs/CsFAMA device shows no obvious degradation in Jsc and FF even after 6000 h storage, unlike the CsFAMA device (Figure S4). We notice in Figure S4a−c that for the pristine CsFAMA-based device, performance degradation is mostly caused by a decrease in Jsc and FF, while for the MAPbI3 NPs/CsFAMA device, Jsc and FF decrease marginally. Remarkably,
both devices almost retain their initial $V_{oc}$ in the period. We observed that the color of the MAPbI$_3$ NPs/CsFAMA device became considerably lighter after 6000 h storage, which is mainly due to phase transition, associated with a decrease in $J_{sc}$ (Figure S4a). In addition, phase transition induces changes in the film morphology and the interface, resulting in a decreased FF. Both light-soaking and moisture stability are enhanced in the high-quality perovskite film grown using the MAPbI$_3$ NP seed-mediated approach. We further investigated the effectiveness of the incorporation of MAPbI$_3$ NP seeding for the growth of a MAPbI$_3$ film, which shows an enhancement of $J_{sc}$ (Figure 9a) and notable light-soaking stability (Figure 9b). The FS and RS $J$–$V$ curves and IPCE spectra of the pristine MAPbI$_3$ and MAPbI$_3$ NPs/ MAPbI$_3$ devices are shown in Figure S5a,b. More importantly, $J_{sc}$ was improved, retaining a similar trend as MAPbI$_3$ NPs/CsFAMA PSCs. This improvement is provided by the MAPbI$_3$ seeding NPs embedded in the perovskite for improved light absorption and charge carrier transport and collection. To confirm the reproducibility of the PSC performance, 15 and 24 individual devices based on pristine MAPbI$_3$ and MAPbI$_3$ NPs/MAPbI$_3$ were fabricated, respectively. The average $J_{sc}$, $V_{oc}$, FF, and PCE values of the PSCs were compared (Figure S5c–f and Table S6). The PSCs with the pristine MAPbI$_3$ film exhibit an average $J_{sc}$ of 20.96 ± 1.4 mA/cm$^2$, $V_{oc}$ of 1.0 ± 0.03 V, FF of 0.68 ± 0.05, and PCE of 14.20 ± 1.38%. Conversely, the PSC with the MAPbI$_3$ NPs/MAPbI$_3$ film has an average $J_{sc}$ of 21.89 ± 0.89 mA/cm$^2$, $V_{oc}$ of 1.01 ± 0.03 V, FF of 0.71 ± 0.04, and PCE of 15.64 ± 0.36%. The MAPbI$_3$ NPs/MAPbI$_3$-based PSCs yield better reproducibility and superior PCE compared to the pristine MAPbI$_3$-based devices. Furthermore, the FWHM value of the peak decreases from 0.27 for MAPbI$_3$ to 0.25 for MAPbI$_3$ NPs/ MAPbI$_3$ films, implying higher crystallinity of the MAPbI$_3$ NPs/MAPbI$_3$ films (Figure S6c). Figure S6f shows the grain size distribution histograms of pristine MAPbI$_3$ and MAPbI$_3$ NPs containing the MAPbI$_3$ film. The MAPbI$_3$ NPs/MAPbI$_3$ device presents remarkable light-soaking stability, holding 85% of the initial PCE after 2 h exposure. We attribute these noticeably stabilized light-soaking characteristics to the hydrophobicity (Figure S6b), crystallinity (Figure S6c), and large domains of the IL-aided MAPbI$_3$ NPs/MAPbI$_3$ film (Figure S6e) compared to the pristine MAPbI$_3$ film (Figure S6d). The improved stability of MAPbI$_3$ NP-seeded growth significantly relies on the following features: first, the more hydrophobic IL-aided MAPbI$_3$ NPs slow down the CsFAMA growth, forming large crystal domains with fewer grain boundaries (as evident from the XPS and FTIR spectra; Figure 2a–c), which effectively limit the exposure to moisture. Second, the promoted crystals significantly reduce the degradation of the perovskite (Figure 2d). A similar trend occurs in the case of the MAPbI$_3$ NPs/MAPbI$_3$ device. Therefore, incorporation of the MAPbI$_3$ NP seeds into the pristine MAPbI$_3$ film improves the $J_{sc}$ and light-soaking stability. These results can serve as a guide to further improve the device stability by choosing a more robust HTM.

### CONCLUSIONS

We developed a novel technique based on MAPbI$_3$ NP seeds embedded in conventional CsFAMA or MAPbI$_3$ structures, showing that the IL-aided MAPbI$_3$ NPs significantly promote high-quality perovskite films with large single-crystal domains, improving light harvesting, device performance, and operation stability. The solar cells based on the MAPbI$_3$ NPs/CsFAMA configuration exhibit significant enhancement in both device efficiency and stability over time. In addition, significant improvement of $J_{sc}$ is found in both the MAPbI$_3$ NPs/CsFAMA and MAPbI$_3$ configurations. PSCs using the MAPbI$_3$ NPs/CsFAMA perovskite exhibit a PCE of 19.44%, which is larger than that of pristine CsFAMA (17.33%). PSCs with MAPbI$_3$ NPs/CsFAMA still retain 92% of the original PCE value after light-soaking tests with non-encapsulated devices for ~2 h in the air with high (30–40%) humidity. Meanwhile, the PCE of pristine CsFAMA-based PSCs almost decreased to 83% of the original value, demonstrating that the MAPbI$_3$ NP seed-embedded CsFAMA has superior light-soaking stability. Furthermore, the device based on the MAPbI$_3$ NPs/MAPbI$_3$ structure shows excellent light-soaking stability. The highly hydrophobic IL-aided MAPbI$_3$ NPs/CsFAMA devices are stable against moisture, retaining above 80% of the initial PCE even after 6000 h at ambient (non-encapsulated). Stability is improved in the high-quality perovskite film with large single-crystal domains, which effectively reduce the attack of moisture. The present MAPbI$_3$ NP-seeded growth demonstrates the possibility to further enhance the efficiency and stability of PSCs by sophisticated defect engineering (e.g., interface recombination and trap passivation).

### ASSOCIATED CONTENT

#### Supporting Information

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

UV–vis spectra of the perovskite films formed with MAPbI$_3$ NPs, CsFAMA, and MAPbI$_3$ NPs/CsFAMA. Forward scan (FS) and reverse scan (RS) $J$–$V$ curves of the devices with MAPbI$_3$ NP, CsFAMA, and MAPbI$_3$ NPs/CsFAMA layers. Histogram of PCEs of PSCs comprising the CsFAMA and MAPbI$_3$ NPs/CsFAMA layer. Photovoltaic variables of PSCs fabricated with CsFAMA and MAPbI$_3$ NP containing CsFAMA film: $J_{sc}$, $V_{oc}$ and FF, as a functions of storage periods (h). FS and RS $J$–$V$ features of the devices with pristine MAPbI$_3$ and MAPbI$_3$ NPs embedded MAPbI$_3$ film and IPCE spectra of devices with a pristine MAPbI$_3$ and MAPbI$_3$ NPs embedded MAPbI$_3$ film. Average $J_{sc}$, $V_{oc}$, FF, and PCE values of PSCs fabricated with MAPbI$_3$ NPs/CsFAMA, MAPbI$_3$ NPs/CsFAMA layers. Water contact angle measurements of pristine MAPbI$_3$ film and MAPbI$_3$ NPs embedded MAPbI$_3$ film. XRD spectra of pristine MAPbI$_3$ and MAPbI$_3$ NPs seeding embedded MAPbI$_3$ film. SEM images of pristine MAPbI$_3$ and MAPbI$_3$ NPs/MAPbI$_3$ film. The grain size distribution histograms of pristine MAPbI$_3$ and MAPbI$_3$ NPs containing the MAPbI$_3$ film. Nyquist plots fitting analysis parameters. TRPL spectra of CsFAMA and MAPbI$_3$ NPs/CsFAMA-based perovskite films. Outline of device performance features with MAPbI$_3$ NPs, CsFAMA, and MAPbI$_3$ NPs/CsFAMA-based photosensitive perovskite layers. Summary of device performance characteristics with pristine MAPbI$_3$ and MAPbI$_3$ NPs/MAPbI$_3$ layers (PDF)
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Notes

The authors declare no competing financial interest.

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