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# Single-Crystal-Assisted In Situ Phase Reconstruction Enables Efficient and Stable 2D/3D Perovskite Solar Cells

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ABSTRACT: Perovskite solar cells (PSCs) that incorporate both two-dimensional				24.87%

(2D) and three-dimensional (3D) phases possess the potential to combine the high stability of 2D PSCs with the superior efficiency of 3D PSCs. Here, we demonstrated in situ phase reconstruction of 2D/3D perovskites using a 2D perovskite single-crystalassisted method. A gradient phase distribution of 2D RP perovskites was formed after spin-coating a solution of the 2D Ruddlesden–Popper (RP) perovskite single crystal, (DFP)<sub>2</sub>PbI<sub>4</sub>, onto the 3D perovskite surface, followed by thermal annealing. The resulting film exhibits much reduced trap density, increased carrier mobility, and superior water resistance. As a result, the optimized 2D/3D PSCs achieved a champion efficiency of 24.87% with a high open-circuit voltage  $(V_{\rm OC})$  of 1.185 V. This performance surpasses the control 3D perovskite device, which achieved an efficiency of 22.43% and a  $V_{\rm OC}$  of 1.129 V. Importantly, the unencapsulated device demonstrates significantly enhanced operational stability, preserving over 97% of its original efficiency



after continuous light irradiation for 1500 h. Moreover, the extrapolated  $T_{80}$  lifetimes surpass 5700 h. These findings pave the way for rational regulation of the gradient phase distribution at the interface between 2D and 3D perovskites by employing 2D RP perovskite crystals to achieve stable and efficient PSCs.

# INTRODUCTION

In the past decade, perovskite solar cells (PSCs) have attracted significant attention owing to their remarkable progress.<sup>1-6</sup> PSCs offer several advantages, including low-cost fabrication, long carrier diffusion length, high absorption coefficient, and superior defect tolerance.<sup>7–9</sup> However, their long-term stability remains a major challenge for commercialization. One of the main issues affecting the stability of PSCs is the susceptibility of halide perovskites to various environmental conditions such as heat, moisture, and oxygen.<sup>10-12</sup> Additionally, ionic constituents within perovskite materials are particularly prone to migrating in response to external stimuli, primarily due to their low activation energy for ionic migration.<sup>13</sup> This can result in undesired ion redistribution or phase separation, particularly in mixed halide perovskites, further compromising the long-term stability of PSCs.

Two-dimensional (2D) perovskites, such as 2D Ruddlesden-Popper (RP) perovskites and 2D Dion-Jacobson (DJ) perovskites, are known for their excellent long-term stability characteristics such as hydrophobicity and high formation energy.<sup>14-17</sup> Integrating the 2D perovskite into three-dimensional (3D) perovskite matrices offers the potential to achieve a synergy of high efficiency and stability in PSCs.<sup>18-22</sup> Typically, 2D/3D perovskite heterojunctions could be constructed by either growing a 2D perovskite layer on top/ bottom of a 3D perovskite film or incorporating 2D perovskite within the bulk of the 3D perovskite.<sup>23-27</sup> The incorporated 2D perovskite could passivate the surface or bulk defects, optimize the film morphology, and hinder the ion migration, resulting in reduced trap density and improved device performance.<sup>21,28–32</sup>

So far, one of the most used methods is to deposit an organic ligand layer on top of 3D perovskite to passivate the surface defects and form the 2D/3D perovskite heterojunction. The organic ligands could react with the 3D perovskite or the residual PbI<sub>2</sub> to form 2D perovskites with different *n*-values on the surface of 3D perovskites.<sup>33</sup> However, the formation of 2D perovskites with different n-values can lead to inconsistent energy band alignment (type I or type II) at heterojunctions, which negatively impacts device performance.<sup>34</sup> This limitation has made it crucial to precisely control the phase distribution of the 2D perovskite passivation layer to regulate energy level alignment. Mohite et al. demonstrated an approach using an RP 2D BA2MA2Pb3I10 single crystal on the surface of 3D perovskites to form a phase-pure 2D passivation layer,

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**Figure 1.** (a) 3D molecular structure of DFPI. (b, c) Single-crystal structure of the  $(DFP)_2PbI_4$  perovskite. (d) SEM images of layered  $(DFP)_2PbI_4$  crystals. (e) I 3d core level X-ray photoelectron spectra (XPS) of the control, target-1, and target-2 films. (f) Pb 4f core level XPS spectra of the control, target-1, and target-2 films. (g) N 1S core level XPS spectra of the control, target-1, and target-2 films.

achieving an excellent efficiency of 24.5%.<sup>35</sup> However, it is a complex process to obtain 2D perovskite single crystals with different nanometer values to passivate the 3D perovskite surface. Additionally, 2D/3D heterojunctions with a gradient-ordered distribution could be more favorable for energy band bending, which facilitates charge transport. Therefore, there is an urgent need to develop a simple and practical strategy to modulate the phase distribution of 2D perovskite passivation layers, enabling better control over the energy level alignment and overall device performance.

In this work, we developed an in situ phase reconstruction strategy of 2D/3D perovskites using a method assisted by 2D perovskite single crystals. Specifically, using an in situ grazing incidence wide-angle X-ray scattering (GIWAXS) measurements, we observed a gradient distribution of 2D perovskites on the surface of a 3D perovskite by depositing a solution of 2D RP perovskite, (DFP)<sub>2</sub>PbI<sub>4</sub> single crystal, based on a 4,4-difluoropiperidine (DFP) spacer onto it under subsequent annealing. Devices that are based on these 2D/3D perovskites exhibit an impressive efficiency of up to 24.87% with extrapolated  $T_{80}$  operational lifetimes exceeding 5500 h.

#### RESULTS AND DISCUSSION

Figure 1a illustrates the 3D chemical structure of the DFP spacer. The single-crystal structure of the 2D perovskite  $(DFP)_2PbI_4$  was grown in a mixture of PbO, DFPI, hydriodic acid, and hypophosphorous acid by cooling the solution slowly from 130 °C to room temperature. The crystallographic data pertaining to this structure are summarized in Table S1. Note that the  $(DFP)_2PbI_4$  crystals can also be obtained through an alternative method involving PbI<sub>2</sub>, DFPCl, and HI.<sup>36</sup> As depicted in Figure 1b, the bond length of NH…I was 2.815 Å, which is shorter than the sum of the van der Waals radii (vdW) of H and I atoms (~3.1 Å). This observation suggests robust

hydrogen-bonding interactions between -NH<sub>3</sub><sup>+</sup> in DFP and I in the corner-sharing  $[PbI_6]^{4-}$  layer. The intermolecular CH... F distances were found to be 3.524 and 2.521 Å, respectively. The shortest CH…F distance of 2.521 Å is shorter than the sum of vdW (2.67 Å) of F and H, indicating the presence of CH…F hydrogen-bonding interactions.<sup>37</sup> The penetration distance of nitrogen can serve as an estimate of the strength of the electrostatic interaction between the negatively charged inorganic layers and the positively charged tail of the organic spacer.<sup>38</sup> The nitrogen atoms in the DFP spacer are sunk into the cavity of the corner-sharing  $[PbI_6]^{4-}$  layer with the same depth of 0.465 Å (Figure S1). These numerous noncovalent interactions could augment the structural stability of the 2D RP perovskite, facilitating the subsequent formation of stable 2D/3D structures. The scanning electron microscopy (SEM) image of the (DFP)<sub>2</sub>PbI<sub>4</sub> perovskite shows the layered structure characteristic of the 2D perovskite (Figures 1d and S2).

To optimize the growth kinetics of 3D perovskite, we introduced the (DFP)<sub>2</sub>PbI<sub>4</sub> single crystal as seeds into the FA<sub>0.95</sub>MA<sub>0.05</sub>PbI<sub>3</sub> precursor, which we referred to as target-1. The acetonitrile solution of the (DFP)<sub>2</sub>PbI<sub>4</sub> single crystal was deposited onto the surface of the target-1 film to passivate surface defects and modulate energy level alignment. We denoted this modified film as target-2. X-ray photoelectron spectroscopy (XPS) was conducted to study the chemical state of surface elements in the perovskite. In Figure 1e, two dominant I 3d peaks were observed for the control film at 618.51 eV (I  $3d_{7/2}$ ) and 629.36 eV (I  $3d_{5/2}$ ). These peaks exhibit a shift to 618.30 and 617.68 eV, respectively, for both target-1 and target-2 films. The I 3d peaks of target-1 and target-2 films shifted toward lower binding energy compared to the control samples. This shift could be attributed to the formation of N-H…I hydrogen bonds between DFPI and



**Figure 2.** (a–c) Surface (up) and cross-sectional (down) SEM images of the control (a), target-1 (b), and target-2 (c) perovskite films. (d) X-ray diffraction (XRD) pattern from control 3D, target-1, and target-2 films. (e) Statistical distribution of surface potential extracted from the Kelvin probe force microscopy (KPFM) images. (f) Energy level scheme for the control and target-1 films extracted from ultraviolet photoelectron spectroscopy (UPS) data. The  $E_F$  was obtained from =  $h\nu - (E_{cutoff} - E_F)$ .

 $[PbI_6]^{4-}$  octahedra. The shift of Pb 4f and N 1S represents the same trend of I 3d (Figures 1f,g and S3).

To investigate the effect of 2D RP perovskite (DFP)<sub>2</sub>PbI<sub>4</sub> crystal seeds on film morphology, we conducted dynamic light scattering (DLS) measurements on the respective precursor solutions. As illustrated in Figure S4, precursor aggregates were identified with a primary size of less than 600 nm in the control perovskite solution and approximately 1  $\mu$ m in the target-1 perovskite precursor solutions. These aggregates in the precursor solution directly influence nucleation density and the obtained grain size, which was verified by the SEM images of the corresponding films.<sup>39</sup> As shown in Figures 2a and S5, the average grain size of the control film is about 1.2  $\mu$ m, exhibiting obvious holes that are detrimental to the long-term stability of the device. In contrast, the target-1 and target-2 films displayed larger grain sizes (~2.0  $\mu$ m), resulting in a reduction in the number of grain boundaries and voids. The cross-sectional SEM of target-1 and target-2 films, shown at the bottom of Figure 2b,c, reveals vertically penetrating crystals and fewer grain boundaries compared to the control film, leading to a reduction in the defect density as discussed below. Furthermore, we can clearly observe that the 2D perovskites grow uniformly on the surface of 2D/3D perovskites with a thickness of ~19.7 nm (Figure S6). The improved film quality of target-1 and target-2 films in comparison with the control film was further verified by the atomic force microscopy (AFM) measurements (Figure S7). The root-mean-square roughness of the perovskite films was effectively reduced from

58.1 nm for the control film to 25.7 nm for the target-1 and 20.5 nm for the target-2 films.

X-ray diffraction (XRD) measurements were performed to study the crystallinity of the perovskite films (Figure 2d). A noticeable change was observed for two diffraction peaks at 14.28 and  $28.51^{\circ}$ , corresponding to the (110) and the (220) planes of the control perovskite film, respectively. The (110) peak exhibits a shift toward lower angles of 14.26° for the target-1 film and 14.14° for the target-2 film (Figure S8a). This shift suggests the incorporation of 2D perovskite into the 3D perovskite crystal lattice, leading to a lattice expansion.<sup>40</sup> The target-1 and target-2 films exhibited a much stronger intensity of the (110) peak compared with the control film, indicating that the 2D (DFP)<sub>2</sub>PbI<sub>4</sub> perovskite seed promotes the crystal growth of the perovskite film. Additionally, a diffraction peak appeared at below 10° for the target-2 film, suggesting that the existence of 2D perovskite phases paralleled to the substrate. The two peaks observed in the target-2 film at 4.66 and 8.96° could be assigned to the (020) and (040) phases of 2D perovskite with n = 2 (Figure S9 and Table S2), respectively, which were further verified by GIWAXS measurements below. Note that the slightly increased PbI<sub>2</sub> peak at around 12.8° (Figure S8b) may be related to the thermal annealing-induced reaction between 2D perovskite (DFP)<sub>2</sub>PbI<sub>4</sub> and the underlying 3D perovskites.

The surface potential images, measured using Kelvin probe force microscopy (KPFM), reveal a more uniform morphology for the target-1 and target-2 films compared with that of the control film (Figure S10). As shown in Figure 2e, in contrast to

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**Figure 3.** (a-c) Schematic of in situ GIWAXS characterization, illustrating the deposition of  $(DFP)_2PbI_4$  perovskite on 3D perovskite by a spincoating and annealing process under 100 °C. (d) Photoluminescence (PL) spectra of the 3D perovskite thin films after deposition with  $(DFP)_2PbI_4$ perovskite under 100 °C. (e) Angle-dependent GIWAXS pattern of the target-2 with annealing for 5 min. (f) The schematic energy band diagrams after the  $(DFP)_2PbI_4$  perovskite treatment and the forming of the graded heterojunction. (g) Schematic illustration of the structural evolution mechanism of  $(DFP)_2PbI_4$  perovskite on the 3D perovskite surface based on thermal stress-guided growth.

the control film, the target-1 and target-2 films exhibit an increased potential from 20 to 40 mV for the target-1 film and 60 to 100 mV for the target-2 film. The enlarged surface potential indicates that their Fermi levels ( $E_f$ ) are closer to their conductive band (CB) edge,<sup>41</sup> aligning with the findings from ultraviolet photoelectron spectroscopy (UPS) results (Figure S11). In Figure 2f, the  $E_f$  value relative to the valence band maximum (VBM) changes from 0.43 eV for the control to 0.39 eV for target-1 and 0.37 eV for target-2 films, indicating a more p-type characteristic of the surface in the target-2 film. This characteristic could facilitate efficient charge extraction and transport from perovskite to hole transport layer (HTL).

In situ GIWAXS was employed to characterize the microscopic changes of the  $(DFP)_2PbI_4$ -capped 2D/3D perovskite surface during a thermal aging process. As shown in Figures 3a-c and S12, we monitored the evolution of the

2D (DFP)<sub>2</sub>PbI<sub>4</sub> layer on the 2D/3D perovskite surface during heating at 100 °C. The 2D (DFP)<sub>2</sub>PbI<sub>4</sub> perovskite was observed on the 2D/3D perovskite surface prior to heating (Figure 3a). We presume that the preheating step was utilized to remove the solvent from the passivation layer. Upon subsequent annealing, the signal for the n = 2 phase first appears at  $q_z = 0.32$  nm<sup>-1</sup> after 60 s (Figure 3b), followed by the n = 3 phase that appears at  $q_z = 0.76$  nm<sup>-1</sup> after 300 s (Figure 3c). To investigate the distribution of the low-*n*-value phases, we determined the formed low-*n*-value phases of n = 1, 2, 3 through UV–vis absorption spectrum (Figure S13), which shows the corresponding absorption peaks at 518, 578, and 613 nm, respectively.

To further validate the change in the n value of 2D perovskite after capping on a 2D/3D perovskite surface under thermodynamic action, we performed an in situ PL test (Figure



**Figure 4.** (a) J-V scan of the control, target-1, and target-2 PSCs. (b) PCE and  $V_{OC}$  of the corresponding devices. (c) The Mott–Schottky plots for the corresponding devices. (d) EQE spectra and integrated  $J_{SC}$  of the corresponding devices. (e)  $V_{OC}$  versus light intensity for the corresponding devices. (f) Time-resolved PL (TRPL) spectra of the control, target-1, and target-2 films. (g–i) TRES of the control (g), target-1 (h), and target-2 (i) films.

3d). In the case of unannealed samples, only n = 1 phase of 2D perovskite is present on the perovskite surface, and subsequently, n = 2 and 3 2D perovskite phases emerge as the heating time increases. Additionally, as the annealing time was further extended, no new peaks appeared, which is in good agreement with the GIWAXS results. Note that no such phenomenon was observed when employing a DFPI solution instead of  $(DFP)_2PbI_4$  for spin-coating onto the target-1 perovskite film (Figure S14).

Through GIWAXS measurements with varying X-ray incidence angles ranging from 0.1 to 0.2° on the target-2 film, we made an interesting experimental observation (Figures 3e and S15). Changing the incidence angles during GIWAXS measurements allows penetration to various depths within the 2D/3D perovskite films, thereby allowing the detection of distinct 2D structural distributions. As shown in Figures 3e and S15, at an incidence angle of 0.1°, the GIWAXS pattern displayed a diffraction peak at q = 0.52 nm<sup>-1</sup> along the *z*-direction, corresponding to the (002) plane of the layered (DFP)<sub>2</sub>PbI<sub>4</sub> phase. This plane is parallel to the substrate, with a layer spacing of ~11.89 Å, indicating the presence of the n = 1 2D perovskite phase on the top layer of the 2D/3D perovskite structure. As the incidence angle increased, the

signal for n = 2 (020) phase emerged at  $q_z = 0.32$  nm<sup>-1</sup>, and at an incidence angle of  $0.16^\circ$ , the signal for n = 3 (060) appeared at  $q_z = 0.76 \text{ nm}^{-1}$ , as verified by the XRD patterns of 2D perovskite  $(DFP)_2FA_{n-1}PbnI_{3n+1}$  with different *n*-values (Figure S9 and Table S2). This suggests the existence of a top-to-bottom gradient distribution of the n value within the 2D/3D perovskite structure. Considering the band bending at the gradient junction, the energy levels can be illustrated in Figure 3f. After the in situ generation of 2D/3D hybrid perovskites with a vertical gradient distribution, the VB and CB of the target-2 film increased to -5.12 and -4.38 eV, forming a stepped energy level. In the 3D perovskite film, the upward band bending can hinder electron transport to the HTL, while the 2D interface bends downward, facilitating hole extraction at the interface. Consequently, a gradient heterojunction indeed facilitates hole extraction and reduces charge recombination at the interface.<sup>42</sup> Therefore, under thermodynamic conditions, the reaction occurs between the (DFP)<sub>2</sub>PbI<sub>4</sub> on the top layer and 3D perovskite (FAPbI<sub>3</sub>) underneath, causing the reconstruction of the perovskite surface. We speculate that the main reactions on the surface of the 2D layer-capped 2D/3D perovskite are as follows



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**Figure 5.** (a) Photographs of control (left) and target-2 films (right) immersed in water for 0 and 10 s. (b) Aging test of the unencapsulated devices stored in air (RH, 45  $\pm$  5%). (c) Aging test of the unencapsulated devices under constant heating at 80 °C in N<sub>2</sub>. (d) Maximum power point (MPP) tracking of the unencapsulated devices unstimulated AM1.5 illumination, 100 mW cm<sup>-2</sup> in a nitrogen atmosphere at 60 °C.

$$(FAPbI_3) + (DFP)_2PbI_4 = (DFP)_2(FA)Pb_2I_7$$

$$(FAPbI_3) + (DFP)_2(FA)Pb_2I_7 = (DFP)_2(FA)_2Pb_3I_{10}$$

As illustrated in Figure 3g, a growth model was tentatively proposed to describe the formation of the vertical distribution of the 2D perovskites. First, an acetonitrile solution of the  $(DFP)_2PbI_4$  crystal was deposited and uniformly covered on the 3D perovskite surface using a spin-coating method. Subsequently, (DFP)<sub>2</sub>PbI<sub>4</sub> reacts in situ with FAPbI<sub>3</sub> during the thermal annealing process to form  $n = 2 \text{ (DFP)}_2\text{FAPb}_2\text{I}_5$ perovskite. The (DFP)<sub>2</sub>FAPb<sub>2</sub>I<sub>5</sub> continues to react with FAPbI<sub>3</sub> underneath and form  $(DFP)_2FA_2Pb_3I_7$  perovskite (*n* = 3). This vertically distributed 2D/3D structure, on one hand, facilitates energy level alignment and reduces charge carrier recombination loss at the interface between the perovskite and HTL. On the other hand, the 2D perovskite on the surface of the 3D perovskite film can protect it from moisture erosion and increase the long-term stability of the device due to its hydrophobic nature.

The current density–voltage (J-V) curves of n–i–p-type PSCs are shown in Figure 4a. The photovoltaic parameters of the devices optimized under various conditions are outlined in Tables S3 and S4. The control device exhibits a low power conversion efficiency (PCE) of 22.43%, with an open-circuit voltage ( $V_{\rm OC}$ ) of 1.129 V, a short-circuit current density ( $J_{\rm SC}$ ) of 24.88 mA cm<sup>-2</sup>, and a fill factor (FF) of 79.84%. The PCE of the target-1 devices improved to 23.06%, attributed to enhanced film quality and decreased nonradiative recombina-

tion loss. Additionally, we investigated the effect of different annealing times of perovskite films after capping a passivation layer on the device performance. With annealing times of 0, 1, and 5 min, the corresponding target-2 devices achieved a PCE of 23.44, 24.16, and 24.87%, accompanied by a notably increased V<sub>OC</sub> of 1.167, 1.171, and 1.185 V, respectively. In contrast to the contrast device, the improved  $V_{OC}$  of the target-1 and target-2 devices (Figure 4b) was further verified by the capacitance-voltage (C-V) characterization according to the Mott-Schottky relationship (Figure 4c).<sup>43</sup> The built-in potential  $(V_{\rm bi})$  is 1.06 V for control, 1.10 V for target-1, and 1.14 V for target-2 devices, aligning with the increasing trend of  $V_{\rm OC}$  in the J-V curves. The elevated  $V_{\rm bi}$  signifies a greater driving force for more efficient charge transport and collection, resulting in a higher  $V_{\rm OC}$  in target-2 devices. Note that when further increasing the annealing time to 10 min, the PCE and  $V_{\rm OC}$  of target-2 device were decreased to 23.07% and 1.177 V, respectively. The steady-state power output of the devices in Figure S16 shows that the control, target-1, and target-2 devices display a steady-state PCE of 20.93, 22.06, and 24.07%, respectively, after continuing 1 sun illumination over 90 s, aligning well with the J-V results. The integrated current densities obtained from the external quantum efficiency (EQE) in Figure 4d are 24.36 mA cm<sup>-2</sup> for control, 24.61 mA cm<sup>-2</sup> for target-1, and 24.95 mA cm<sup>-2</sup> for target-2 devices, in good agreement with the J-V results.

Figure 4e illustrates seminatural logarithmic plots of  $V_{OC}$  as a function of light intensity for the devices along with slopes obtained through linear fitting of the data. The slope from kT/

q reflects trap-induced recombination, where k is Boltzmann's constant, T is the absolute temperature, and q is the elementary charge. The target-1 and target-2 perovskites exhibit lower slopes of 1.95 and 1.05 kT/q, respectively, compared to a slope of 2.41 kT/q for the control device. The much lower slope of target-2 devices demonstrates the suppression of charge carrier recombination due to the reduced trap density as confirmed by the space-charge-limited current (SCLC) method.<sup>44–46</sup> The trap density  $(N_t)$  and mobility ( $\mu$ ) were obtained from the dark current–voltage (*J*– V) curve (Figure S18a). The electron trap density calculated from SCLC data decreased from  $1.31 \times 10^{17}$  cm<sup>-3</sup> for the control film to  $2.81\times10^{16}$  and  $1.39\times10^{16}~\text{cm}^{-3}$  for target-1 and target-2 films, respectively. Similarly, the hole trap density decreased from  $8.06 \times 10^{16}$  cm<sup>-3</sup> for the control film to  $3.36 \times$  $10^{16}$  cm<sup>-3</sup> for the target-1 film and  $1.65 \times 10^{16}$  cm<sup>-3</sup> for the target-2 film. These results indicate that the synergistic effect of seed-induced growth and surface gradient passivation effectively reduces surface and bulk defects, resulting in increased  $V_{\rm OC}$  of the corresponding devices.

We performed transient photovoltage decay (TPV) and transient photocurrent decay (TPC) measurements to evaluate the charge carrier dynamics in the respective devices under operational conditions. The TPV (Figure S19a) curve shows a charge recombination time constants ( $\tau$ ) of 294.5  $\mu$ s for the target-2 device, which decreases to 88.3  $\mu$ s for target-1 and 29.5  $\mu$ s for control devices. This suggests an enhanced carrier lifetime in the target-2 device due to reduced nonradiative recombination.<sup>31</sup> In Figure S19b, it is evident from the TPC curves that the TPC decay time of the target-2 device is 1.84  $\mu$ s, which is significantly lower than that of the control device ( $\tau = 2.26 \ \mu$ s), signifying an enhanced charge collection efficiency.

The steady-state photoluminescence (PL) spectra and timeresolved PL decay curves were used to elucidate the effect of the 2D (DFP)<sub>2</sub>PbI<sub>4</sub> perovskite on the carrier lifetime of the corresponding perovskite films. As shown in Figure S20, the target-1 film exhibits a higher PL intensity due to the higherquality 3D perovskite film induced by the  $(DFP)_2PbI_4$  seeds. Moreover, the PL intensity of the target-2 film is further enhanced, suggesting that nonradiative recombination is further inhibited with surface gradient passivation. Figure 4f displays the time-resolved PL (TRPL) spectra, which show a significantly long bulk carrier lifetime of 4.26  $\mu$ s for the target-1 film. This is nearly 8 times greater than that of 0.56  $\mu$ s observed in the control film, suggesting significantly reduced bulk defects in the target-1 film with the 2D (DFP)<sub>2</sub>PbI<sub>4</sub> seed.<sup>38</sup> After the 2D perovskite (DFP)<sub>2</sub>PbI<sub>4</sub> treatment, the carrier lifetime of the target-2 film further increases to 5.91  $\mu$ s, indicating that vertically distributed 2D passivation layers can further suppress the interfacial nonradiative recombination by reducing the surface defects. As shown in Figure 4g-i, the target-2 and target-1 films exhibit longer PL lifetimes in the light-emitting range of 775-825 nm, which is consistent with the above test results.

Meanwhile, the target-2 device with an active area of 1.0 cm<sup>2</sup> was also manufactured to assess their homogeneity (Figure S25). A high efficiency of 21.79% was achieved, accompanied by a  $V_{\rm OC}$  of 1.179 V, a  $J_{\rm SC}$  of 24.85 mA cm<sup>-2</sup>, and an FF of 74.37%. The presence of 2D perovskite on the 3D perovskite surface serves as a protective layer, safeguarding the films from moisture, owing to its inherently hydrophobic nature. We further evaluated humidity stability by immersing the perov-

skite films in water (Figure 5a and Supporting Information Videos S1 and S2). The control film turned completely yellow in 10 s, indicating complete decomposition into PbI<sub>2</sub>. In contrast, the onset of perovskite decomposition in the target-2 film was delayed to 20 s. These findings demonstrate that the 2D (DFP)<sub>2</sub>PbI<sub>4</sub> perovskite significantly enhances the humidity stability of the perovskite films. To study film stability in a real outdoor environment, we subjected the control, target-1, and target-2 films with ITO/glass/SnO2 substrates to direct exposure to ambient air (RH,  $45 \pm 5\%$ ) under natural light, tracking them using XRD measurements. As illustrated in Figure S21, an obvious PbI<sub>2</sub> peak appeared in the control perovskite film after 20 days, indicating film decomposition. In contrast, both target-1 and target-2 films exhibited enhanced stability, with minimal PbI<sub>2</sub> being observed after 20 days. Notably, the stability of the target-2 film surpassed that of the target-1 film, attributing to the passivation of surface defects in the perovskite film by  $(DFP)_2PbI_4$ .

To further access the stability of the devices, we subjected the control, target-1, and target-2 devices to various conditions. As shown in Figures 5b and S22, the PCE of the control device decreased to 60.14% of its initial efficiency after exposure to air (RH,  $45 \pm 5\%$ ) for 2500 h. In contrast, the target-1 and target-2 devices maintained 83.15 and 90.70% of their original PCE, respectively, indicating a substantial improvement in humidity stability. Figures 5c and S23 show the normalized PCE of the control, target-1, and target-2 devices under constant heating at 80 °C in N<sub>2</sub>. After 2000 h, the target-2 devices retained 92.10% of their original PCE, while the control and target-1 devices dropped to 64.99 and 79.26% of their initial value after 1000 h, respectively. The superior stability of the target-2 device could be attributed to the improved film stability discussed above. The 2D (DFP)<sub>2</sub>PbI<sub>4</sub> perovskite significantly enhances the quality of perovskite films, and the in situ formation of a passivation layer with a vertical gradient further improves the long-term stability of the perovskite devices. The enduring operational stability of unencapsulated devices was evaluated through continuous maximum power point (MPP) tracking under a white light-emitting diode (LED) illumination (100 mW cm<sup>-2</sup>) in N<sub>2</sub> at 60 °C (Figure 5d). After 1000 h of continuous testing, the control device experienced a reduction to approximately 45% of its initial PCE, whereas the target-1 and target-2 devices sustained over 89 and 97% of their original efficiency after 1500 h, respectively. Exploration of long-term stability in PSCs was achieved through linear decay for predicting device life span.<sup>47,48</sup> As shown in Figure S24, the target-2 device exhibits an extrapolated  $T_{80}$  lifetime of 5761 h. The robust stability of the target devices under various conditions could be attributed to the enhanced film stability, characterized by reduced grain boundaries, improved hydrophobicity, and inhibited ion migration, resulting from the treatment with 2D  $(DFP)_2PbI_4$  perovskite.

#### CONCLUSIONS

In summary, we have successfully demonstrated a very effective strategy for fabricating high-quality 2D/3D perovskite films by developing a single-crystal-assisted surface in situ phase reconstruction method. In this method, a surface heterojunction with a vertical gradient orientation was formed by adjusting the annealing time following the deposition of a solution of a 2D perovskite (DFP)<sub>2</sub>PbI<sub>4</sub> crystal onto the surface of the bulk 2D/3D hybrid perovskite (target-1). The resulting target-2 films showed high film quality with larger

grain sizes, resulting in reduced trap density. In situ GIWAXS analysis confirmed the presence of gradient-distributed 2D passivation layers on the perovskite surfaces through thermodynamic action. Consequently, the target-2 devices achieve a champion PCE of 24.87% with a high  $V_{\rm OC}$  of 1.185 V, significantly surpassing that of the control device, which exhibits a PCE of 22.43% and a  $V_{\rm OC}$  of 1.13 V. Importantly, the target-2 device displays significantly improved operational stability, sustaining over 97% of its original efficiency after 1500 h with an extrapolated  $T_{80}$  lifetime of 5761 h. This innovative approach provides valuable insights for further enhancing the efficiency and stability of 2D/3D PSCs.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c12446.

Brief crystal growth method, device fabrication and characterization, and stability measurements, (Figures S1–S25 and Tables S1–S7) (PDF)

Evaluated humidity stability by immersing the perovskite films in water (Videos S1 and S2) (MP4)

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All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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