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Deciphering 2D perovskite's role in perovskite
solar cells *via* intact 3D/2D junctions†Seungmin Lee, ^{‡a} Hyeonah Cho, ^{‡a} Sohyun Kang,^a Oui Jin Oh,^a Dong Hyun Kim^a
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To advance perovskite solar cells (PSCs) beyond their present efficiency threshold, it is essential to meld device-centric insights with strategies addressing defect passivation issues. Given that 2-dimensional (2D) perovskite, which is commonly utilized to control defects in light-harvesting layers, is used, understanding 3D/2D junctions is crucial for effective device design, as an electric field can be induced at this junction. In this study, we introduce that understanding with the formation of an intact 3D/2D bilayer using (BA)₂PbBr₄ (BA: butylammonium) with deeper work functions, leading to a certified performance of 25.4% compared to (BA)₂PbI₄. While the optoelectronic and defect-related characteristics did not significantly change in accordance with 2D perovskites, an enhancement in built-in potential was observed in the device, which was attributed to the work function of the 2D perovskites. Additionally, through analysis of the p–p isotype heterojunction, it was observed that the built-in potential formed by (BA)₂PbI₄ exists in the 2D layer, whereas the introduction of (BA)₂PbBr₄ shifted the formation of the built-in potential to the 3D layer. The device with a 3D/(BA)₂PbBr₄ heterojunction maintained 89% of its stabilized efficiency after 770 hours in a long-term operational test under 1-sun conditions. The stability of the device, as well as its efficiency, was improved at 85 degrees, offering valuable strategies for the development of high-performance and reliable PSC junctions.

Broader context

Perovskite solar cells have achieved impressive efficiencies of up to 26.1%. A universally adopted strategy for this is forming a 2D perovskite layer on the surface of the 3D light-absorbing perovskite, thereby creating a bilayer 3D/2D structure. Traditionally, 2D surface treatments were used to reduce surface defects in solar cells, with various induced halide salts applied to further minimize these imperfections. In this study, using a distinct intact 3D/2D bilayer structure without any interference between layers and with a clear composition, we discovered that the difference in work function between 3D and 2D perovskites directly influences not just the internal electric field but also efficiency. Additionally, it was discovered that this 2D design not only increased the built-in potential but also altered the distribution of the electric field throughout the device. By amplifying this internal electric field, we successfully developed solar cells with efficiencies exceeding 25%, exhibiting operational and thermal stability. As a 3D/2D bilayer structure is crucial for high efficiency in PSCs regardless of their individual structures, we emphasize that controlling the 3D/2D junction enhances the built-in potential, rather than just mitigating defects.

Introduction

Solar cells, including halide perovskite solar cells (PSCs), function as straightforward photoelectronic devices, first converting photons into photo-generated carriers, and subsequently extracting these

carriers. In all solar cells, to enhance the power conversion efficiency (PCE), prevailing strategies can be grouped into two main categories: the improvement of the quality of the light-harvesting layer and refinement of device design.^{1–6} These methodologies have been continually researched and developed to align with the state-of-the-art standards for each respective type of solar cell. For high-quality single-crystalline solar cells where the light-harvesting layer has already achieved optimal quality, the focus has shifted towards researching aspects of device design. Innovative examples of device design include the integration of back surface fields in GaAs solar cells and the introduction of heterostructures with intrinsic thin layers in c-Si solar cells.^{7–12} When these specialized designs

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were applied to high-quality single-crystalline light-harvesting layers, they significantly enhanced the PCE.

Similarly, PSCs, which have already surpassed a PCE of 26.1%,¹³ consistently focus on enhancing the quality of perovskite films. Efforts in this direction include incorporating additives into the perovskite film, such as formamidinium formate and propylammonium chloride, and passivating the film surface with agents like octylammonium bromide or phenylethylammonium iodide.^{14–18} (Pseudo)halide salts have commonly been used as additives and surface agents in PSCs to enhance the PCE. These halides effectively address halide vacancies in the light-harvesting layer, which is predominantly composed of halides.

Halide materials have been pivotal not only in enhancing quality but also in device design, serving as essential components for the formation of p–n homojunctions, phase heterojunctions, and dimensional heterojunctions.^{19–23} Among these techniques, the three-dimensional/two-dimensional (3D/2D) heterojunction is particularly notable. The 3D/2D junction has always been applied in high-performance PSCs regardless of the solar cell architecture.²⁴ The 3D/2D heterojunction offers a unique advantage by enabling precise control of the built-in potential and band offsets, thanks to the diverse compositions of 2D perovskites.²⁵ Strategies using this heterojunction exert a significant influence on the power output by efficiently managing the flow of photo-generated carriers.

Until now, the creation of 3D/2D heterojunctions has depended mainly on solution processing. The process entails dissolving organic salts, which can form a 2D perovskite through reaction with a 3D surface, in solvents like isopropyl alcohol and applying this solution to the 3D surface to initiate the formation of 2D perovskites.^{26–29} Although the resultant upper quasi-2D layer is formed with compositional uncertainty, the power output is improved.^{30–32} However, it poses challenges in managing the thickness, composition, and crystallinity of the 2D layers, as well as the overall stability of the PSCs. Recent discoveries indicate that acetonitrile, with its suitable dielectric constant and donor strength, supports the growth of phase-pure 2D layers on 3D perovskite without dissolving the underlying layers due to its ability to control thickness and composition.³³ However, as acetonitrile can dissolve quasi-2D materials (a mixture of pure 2D and 3D), there is a risk it might dissolve the underlying 3D perovskite as well. A recent study successfully generated an internal electric field within an intact 3D/2D structure without interference between the 2D and 3D perovskites by using a solid-phase pure 2D (BA)₂PbI₄ thin film.³⁴

However, despite the common approach of 3D/2D halide heterojunctions in PSCs, there remains a significant gap in the fundamental understanding of the precise design methodology for this structure. For instance, while there is information about the stability and the local electric field when various 2D organic cation salts are applied, there is insufficient information on how these electric fields are distributed and vary within the device. Formalizing design rules for 3D/2D heterojunctions will increasingly involve treating each 3D and 2D

layer as a semiconductor and addressing these junctions from a fundamental solid-state physics perspective.

In this study, as we design PSCs with 3D/2D junctions, our goal is to evaluate the impact of changes in the energy levels of the inserted 2D layer on PSC performance while proposing strategies for creating high-performance, viable junctions. Altering the halide in BA-based pure 2D perovskite from iodide to bromide resulted in changes in the bandgap and energy levels. It was also confirmed that this Br-based 2D perovskite can form an intact 3D/(BA)₂PbBr₄ *via* the solid-phase in-plane growth (SIG) method. The formed 3D/(BA)₂PbBr₄ bilayer did not show significant optoelectronic improvement or a reduction in defect density compared to the 3D/(BA)₂PbI₄ bilayer. However, in devices with (BA)₂PbBr₄ inserted, the performance exceeded 25%, compared to the 24% efficiency observed with (BA)₂PbI₄. To analyze this improvement, we utilized the feature of the intact 3D/2D bilayer, whereby each layer is accessible as a semiconductor. We interpreted this junction as a p–p isotype heterojunction and confirmed that the distribution of built-in potential (V_{bi}) induced by the work function (ϕ) of 2D perovskite was significantly different. It was confirmed that in the device with a 3D/(BA)₂PbI₄ junction, the V_{bi} was predominantly applied to the 2D perovskite, whereas in the device with the 3D/(BA)₂PbBr₄ junction, the V_{bi} was primarily formed in the 3D perovskite. The 3D/(BA)₂PbBr₄ device demonstrated a T_{S90} of 730 hours, which is the time it maintained 90% of its stabilized efficiency in a long-term operational stability test. This marks an improvement of more than six times compared to the 118 hours of T_{S90} observed in the standard 3D device. Additionally, it was confirmed that the T_{S90} exceeded 200 hours in a thermal stability test under 85 degrees Celsius involving the introduction of Li-free PTAA.

Results and discussion

Butylammonium-based 2D perovskite properties

For a 3D/2D junction more effective than 3D/(BA)₂PbI₄, it is essential to have a pure 2D perovskite with a deep ϕ to achieve a distinct V_{bi} .³⁵ The energy level of a Ruddlesden–Popper pure 2D perovskite hinges on the relative energy levels between the organic bulky layer and inorganic octahedral layer. Specifically, the energy levels of the bulky organic layer correspond to the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO), whereas the levels of the inorganic layer are characterized by the conduction band minimum (CBM) and valence band minimum (VBM).²⁵ As depicted in Fig. 1a, the energy levels of the BA-based pure 2D family ((BA)₂PbX₄; X = I and Br) predominantly follow the characteristics of the inorganic layer of [PbX₆]^{2–}. This was ascribed to all the energy levels of [PbX₆]^{2–} (represented by solid red and blue lines) being encompassed within the energy levels of the BA organic layer (highlighted in purple). Thus, we noted a change in the energy level when the halide in (BA)₂PbI₄ was replaced with Br. Fig. 1b displays photographs for (BA)₂PbI₄ and (BA)₂PbBr₄ thin films on ITO, both of which

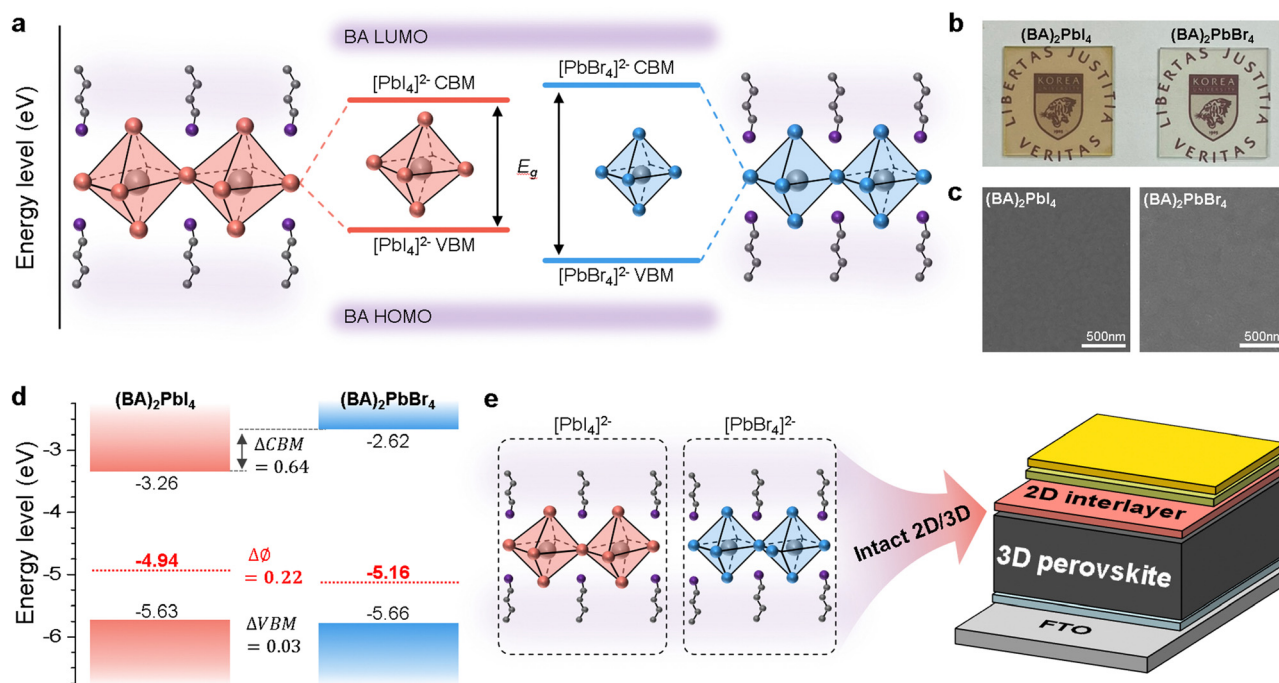


Fig. 1 Butylammonium based Ruddlesden–Popper 2D perovskite film characterization: (a) a schematic illustration of $(\text{BA})_2\text{PbI}_4$ and $(\text{BA})_2\text{PbBr}_4$. The pairs of red lines and blue lines in the band diagrams represent the conduction band minimum and valence band maximum of inorganic $[\text{PbI}_4]^{2-}$ and $[\text{PbBr}_4]^{2-}$ octahedral layers, respectively. The broad, semi-transparent pairs of purple lines correspond to the highest occupied molecular orbital and lowest unoccupied molecular orbital levels of the BA^+ organic layers. (b) Photographs of $(\text{BA})_2\text{PbI}_4$ and $(\text{BA})_2\text{PbBr}_4$ 2D perovskite films on ITO. (c) Top-view SEM images of the 2D perovskite films. Scale bars, 500 nm. (d) Band diagram for $(\text{BA})_2\text{PbI}_4$ and $(\text{BA})_2\text{PbBr}_4$ 2D perovskite films by measuring the UPS and UV-vis by using 2D film on ITO. (e) Schematic illustrations of this work and configuration of the n–i–p perovskite solar cell based on a 3D/2D heterojunction.

were fabricated using solution processing. While the iodide-based pure 2D perovskite film exhibited a yellow color, substitution with Br changed the film color to transparent while maintaining the coverage, as shown in Fig. 1c. To confirm this optical change more clearly, the absorption spectrum was examined. As Br was substituted, a blue shift in the bandgap, similar to that observed in 3D perovskite, was noted (Fig. S1, ESI†).^{36,37} These findings align with the predictions mentioned earlier, and in the BA-based 2D perovskite system, Br substitution plays a crucial role in altering the energy level of the 2D perovskite. Specifically, we conducted photoelectron spectroscopy (UPS) and Kelvin probe force microscopy (KPFM) to examine the specific alterations in the CBM, VBM, and ϕ (Fig. S2, S3, ESI† and Fig. 1d). The $(\text{BA})_2\text{PbI}_4$ film exhibited a CBM of -3.26 eV and a VBM of -5.63 eV, consistent with previous reports.³⁴ The observed ϕ was -4.94 eV, suggesting a p-type nature.³⁸ Upon substitution with Br, the VBM remains similar at -5.66 eV, while the CBM becomes shallower, registering at -2.62 eV. This change suggests that the increased bandgap due to Br substitution predominantly stems from the shift in CBM.^{36,37} Furthermore, the ϕ of -5.16 eV, which is approximately 220 meV deeper than that of $(\text{BA})_2\text{PbI}_4$, highlights the potential for a more substantial internal electrical field in 3D/2D junctions.³⁵ We aimed to assess the impact on solar cell performance and photovoltaic (PV) parameters when using these energy-level designed pure 2D perovskite films as an interlayer (Fig. 1e).

Intact 3D/2D junction properties via 2D perovskites

To design and analyze the internal electrical field in PSCs with a 3D/2D junction, one crucial fundamental prerequisite is paramount: an intact 3D/2D junction between the two semiconductors without compositional interference. Consequently, we designated FAPbI_3 as the 3D perovskite light-harvesting layer, fabricated *via* spin-coating, and later investigated whether $(\text{BA})_2\text{PbBr}_4$ could form an intact 3D/2D bilayer equivalent to that of $(\text{BA})_2\text{PbI}_4$. To evaluate the formation of this intact 3D/2D bilayer, we used the SIG process.³⁴ According to this process, we facilitated the solid-state growth of the 2D perovskite on top of the 3D film. This was achieved by aligning pre-deposited 2D and 3D films surface-to-surface, followed by the application of appropriate heat and pressure. Henceforth, the 2D layer grown on the 3D perovskite surface *via* SIG will be referred to as SIG-2D. For instance, 3D/SIG-I denotes a 3D/2D bilayer where 2D $(\text{BA})_2\text{PbI}_4$ is on top of 3D FAPbI_3 without any composition interference. For further details on the SIG process, kindly refer to the Method section.

Since the growth of the 2D layer can lead to morphological changes, we utilized a scanning electron microscope (SEM) under different conditions. The 3D perovskite exhibits a compact morphology with grain sizes averaging around $1 \mu\text{m}$ (Fig. 2a). Conversely, when the SIG process was applied to $(\text{BA})_2\text{PbI}_4$ and $(\text{BA})_2\text{PbBr}_4$ films, the distinct grains typically observed in 3D perovskites were not evident (Fig. 2b and c).

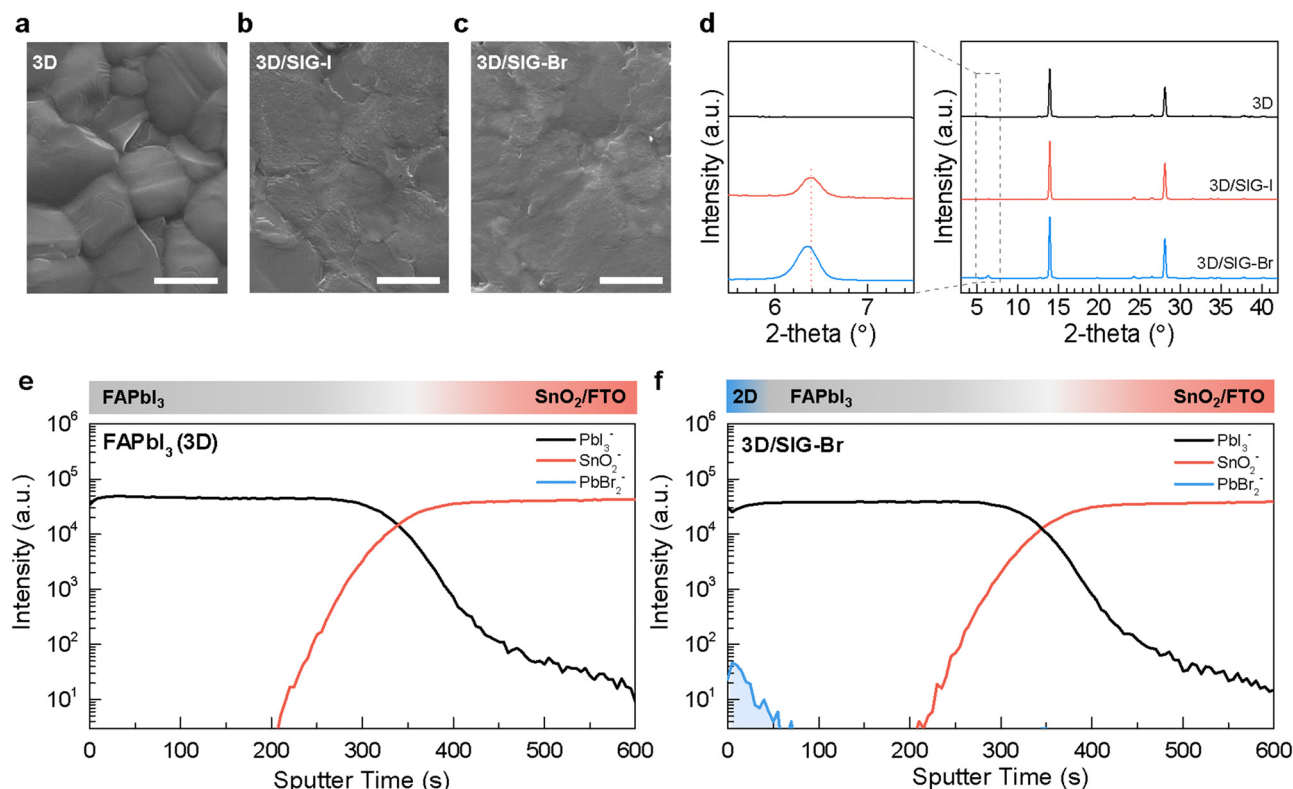


Fig. 2 Intact 3D/2D bilayer film characterization: (a)–(c) top-view SEM images of FAPbI₃, 3D/SIG-I and 3D/SIG-Br. Scale bars, 1 μm. (d) XRD patterns of 3D (FAPbI₃), 3D/SIG-I and 3D/SIG-Br. (e) and (f) ToF-SIMS elemental depth profiles of the perovskite films with different conditions based on the FTO/SnO₂/perovskite structure. Results from negative polarity mode of FAPbI₃ sample and 3D/SIG-Br sample, respectively.

Indeed, the morphology appeared as though something had been newly formed on top of the 3D perovskite. Crystallographic measurements were conducted to identify the specific material that had grown on the surface of this 3D perovskite (Fig. 2d). Under the conditions using (BA)₂PbI₄ and (BA)₂PbBr₄, only new peaks emerging between 6° and 7° were noted, in contrast to the 3D perovskite. These peaks correspond to the (002) crystal plane of each respective 2D perovskite (Fig. S4 and Table S1, ESI†). The measured XRD peak positions of pure 2D perovskite align closely with previously reported data,^{36,39} and the lattice parameters of the 3D perovskite have not changed after forming SIG-I and SIG-Br layers (Table S2, ESI†). These results indicate that the 2D perovskite can grow on the surface and indicate that intact 3D/2D bilayers can be formed even when 2D perovskite is substituted with Br. In fact, exceeding the set temperature range of 60 degrees will result in the formation of a quasi-2D perovskite with an $n = 2$ structure, regardless of whether it involves (BA)₂PbI₄ or (BA)₂PbBr₄ (Fig. S5 and S6, ESI†).

Additionally, we suspected a diffusion phenomenon due to the different halide distributions in 3D/SIG-I and 3D/SIG-Br conditions. The 3D/SIG-I bilayer is composed of FAPbI₃ and (BA)₂PbI₄ films, and both thin films have a single halide, so there is no difference in halide concentration. However, for 3D/SIG-Br, a difference in halide concentration exists between the 3D light-harvesting and 2D layers, suggesting a potential

diffusion of Br into the perovskite bulk. To confirm this hypothesis, we performed time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements (Fig. 2f, g and Fig. S7, ESI†). In the FTO/SnO₂/3D-structured 3D perovskite film, any PbBr₂⁺ signal was detected throughout the measurement period. For thin films under 3D/SIG-Br conditions, the PbBr₂⁺ peak was observed only up to a sputter time of about 60 seconds, and no peak was detected thereafter, like the 3D perovskite film. Depth-dependent X-ray photoelectron spectroscopy (XPS) measurements support the absence of Br diffusion in the 3D/SIG-Br bilayer film (Fig. S8, ESI†). XPS analysis showed a slight decrease in the iodide-to-lead ratio and an increase in the bromide ratio at the surface of the 3D/SIG-Br bilayer (Table S3, ESI†). Ideally, considering the penetration depth, no iodide signals should be detected;⁴⁰ however, due to the decomposition of the perovskite under ultra-high vacuum conditions, clear data were not obtained.^{41–44} To confirm the absence of halide exchange between the SIG-2D and 3D layers, we verified the peak of the (002) crystallographic plane in the pure 2D perovskite with composition (BA)₂PbI_{4–x}Br_x and SIG-2D formed from it. These findings demonstrate that the position of the (002) peak in the SIG-2D layer correlates directly with the composition of the pure 2D perovskite, reaffirming that the composition of SIG-Br is (BA)₂PbBr₄ (Fig. S9, ESI†). Even with halide non-uniformity in this dimensional heterojunction, we determined that a diffusion mechanism does not occur. This

suggests that 3D/SIG-Br and 3D/SIG-I maintain distinct compositions without interlayer interference, allowing them each to be defined as semiconductors.

Defect and performance characterization of the 3D/SIG-2D junction

The quality and behavior of photo-generated charges within the intact 3D/2D halide bilayer were rigorously examined for 3D, 3D/SIG-I and 3D/SIG-Br films. Fig. 3a illustrates that, when measured with an integrating sphere under conditions equivalent to 1-sun illumination, the photoluminescence (PL) spectrum showed an increased PL intensity following the introduction of the 2D layer. To provide a clearer perspective on the quality of isolated and stacked perovskite films, we converted the PL intensity to the absolute photoluminescence quantum efficiency (PLQE) values.^{3,45} The isolated 3D perovskite film exhibited a PLQE of 11.27%. Although the emission

wavelengths remained consistent at 830 nm after stacking 2D perovskite layers, such as (BA)₂PbI₄ and (BA)₂PbBr₄, the PLQE values for the bilayer films 3D/SIG-I and 3D/SIG-Br increased to 16.65% and 18.54%, respectively. Similar findings were observed in the transient properties obtained from time-resolved photoluminescence (TRPL) measurements (Fig. 3b). The stacked perovskite films displayed reduced non-radiative defects, evidenced by their extended carrier lifetimes compared to the isolated perovskite film. Notably, the mono-exponential decays in the tail region showed similar slopes for 3D/SIG-2D bilayer films. Although the interpretation of these slopes varies based on the architecture of isolated and stacked films, the tail lifetime of 3D/SIG-I and 3D/SIG-Br films were notably close, at 3937 and 3990 ns, respectively (Table S4, ESI†). These mono-exponential decay lifetimes allow for estimation of the open-circuit voltage (V_{OC}) of PSCs.^{46,47} For the 3D/SIG-2D junction, the estimated V_{OC} was calculated to be approximately 1.20 V,

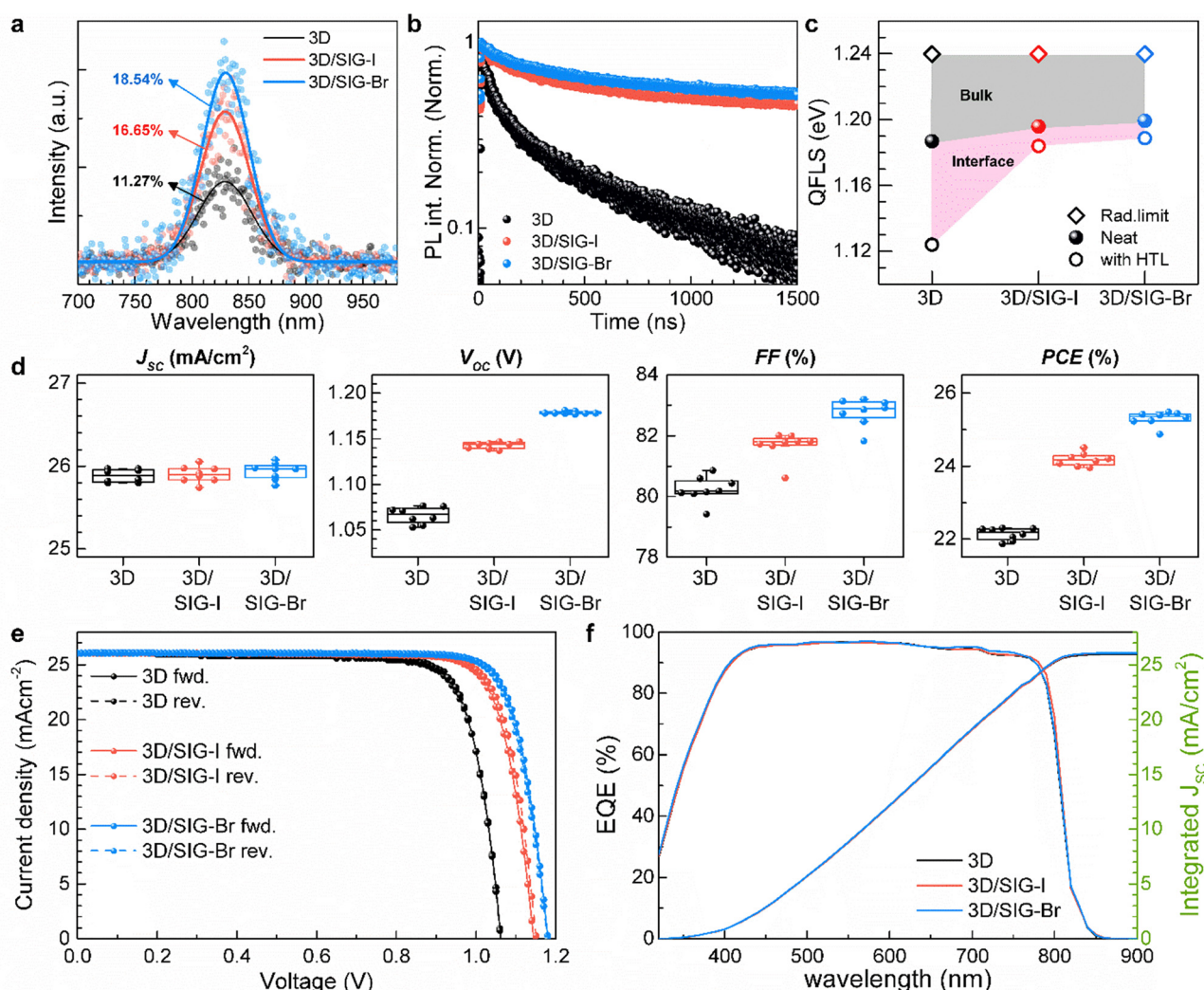


Fig. 3 Reduction of non-radiative defects and PV performance of the devices: (a) steady-state PL spectra and (b) TCSPC decays of the 3D, 3D/SIG-I and 3D/SIG-Br films. (c) Calculated QFLS due to nonradiative recombination. (d) Distribution of J_{SC} , V_{OC} , FF and PCE of all devices. Data are shown for 8 devices of each type made from the same perovskite precursor. (e) J - V curves of champion PSCs with 3D, 3D/SIG-I, and 3D/SIG-Br. 'fwd.' and 'rev.' indicate forward and reverse bias scanning directions, respectively. (f) EQE spectra of the 3D, 3D/SIG-I, and 3D/SIG-Br devices with an integrated J_{SC} of 25.97, 26.05, and 26.08 mA cm⁻², respectively. All devices were fabricated using a structure consisting of FTO/SnO₂/3D/(SIG-2D)/Spiro-OMeTAD/Au.

compared to 1.10 V for 3D film. These findings, obtained from PLQE and TRPL, suggest that the incorporation of 2D layers leads to a reduction of non-radiative defects,^{26,48} while the quality of the interface between the 3D and SIG-2D perovskite layers shows no significant difference irrespective of whether it is SIG-I or SIG-Br. The introduction of the SIG-2D layer resulted in consistent trends in Urbach energy (Fig. S10, ESI†). These findings regarding non-radiative recombination and defect density indicate that the incorporation of a 2D layer on top of the 3D perovskite improves the quality of the light-harvesting layer, but it does not show a significant difference between SIG-I and SIG-Br.

In addition to bulk defects, the interface with the hole-transporting layer can be a significant source of performance degradation.⁴⁹ To evaluate the quality of these interfaces, quasi-Fermi-level splittings (QFLSs) of neat perovskite films (structure: glass/3D/(SIG-2D)) and films stacked with a hole-transporting layer (HTL) (structure: glass/3D/(SIG-2D)/Spiro-OMeTAD) were analyzed (where Spiro-OMeTAD is 2,2',7,7'-tetrakis(*N,N*-di-4-methoxyphenylamine)-9,9'-spirobifluorene) (Fig. 3c). For the neat perovskite (structure: glass/3D/(SIG-2D)), QFLS was calculated to be 1.187, 1.196, and 1.199 eV for 3D, 3D/SIG-I, and 3D/SIG-Br, respectively. The inclusion of the HTL in the 3D film reduced the QFLS to 1.124 eV. For SIG-I and SIG-Br, it is important to note that the QFLSs not only decrease slightly to 1.185 eV and 1.189 eV, respectively, but also that the difference in QFLS between the two types of 2D material is a mere 4 meV. These analyses of HTL interface formation demonstrate that there is no significant difference between SIG-I and SIG-Br based on this interface characteristic.

To determine whether this defect analysis trend persists in PSCs with a 3D/SIG-2D junction, we fabricated a solar cell with a standard structure using SnO₂ and Spiro-OMeTAD as the electron-transporting layer and hole-transporting layer, respectively. The current density–voltage (*J*–*V*) curve was monitored under ambient room-temperature conditions. This was done to analyze the effects of different junction designs on each PV parameter. Fig. 3d presents the statistical distributions of short-circuit current density (*J*_{SC}), *V*_{OC}, fill factor (FF), and PCE, all derived from the *J*–*V* curve. For *J*_{SC}, a similar distribution was observed regardless of the type of SIG-2D layer. Enhancements in *V*_{OC} and FF were observed to vary due to the differing compositions of the SIG-2D layers. The device equipped with 3D/SIG-I exhibited a *V*_{OC} of 1.14 V, which is higher than the 1.07 V observed in the control group (3D). Notably, when SIG-I was replaced with SIG-Br, there was a further increase in *V*_{OC} to an impressive 1.18 V. FF showed improvement as well, increasing to 82% for devices with 3D/SIG-I and further improving to 83% for those with 3D/SIG-Br, compared to the baseline 80% observed in the 3D control group. Consequently, with the incorporation of an SIG-I layer, there was an enhancement in the champion *J*–*V* PCE from 22% (as seen in the control) to 24%. Remarkably, with the insertion of the SIG-Br layer, an efficiency exceeding 25% was measured (Fig. 3e and Table 1). To validate this efficiency, we assessed the steady-state current at the maximum power point for the 3D/SIG-Br PSC and observed a stabilized power output exceeding

Table 1 PV parameters of the 3D, 3D/SIG-I, and 3D/SIG-Br devices. S.D. indicates scan direction

Devices	S.D.	<i>J</i> _{sc} (mA cm ^{−2})	<i>V</i> _{OC} (V)	FF (%)	PCE (%)	R–F average PCE (%)
3D	fwd.	25.97	1.063	80.39	22.18	22.30
	rev.	25.97	1.062	81.33	22.43	
3D/SIG-I	fwd.	26.04	1.145	81.92	24.42	24.52
	rev.	26.06	1.150	82.11	24.61	
3D/SIG-Br	fwd.	26.11	1.181	82.78	25.53	25.47
	rev.	26.05	1.181	82.67	25.42	

25% (Fig. S11, ESI†). As shown in Fig. 3f, external quantum efficiency (EQE) was studied to verify the measured *J*_{SC}, indicating that they all showed similar values regardless of the SIG-2D layer (control: 25.97 mA cm^{−2}; 3D/SIG-I: 26.05 mA cm^{−2}; 3D/SIG-Br: 26.08 mA cm^{−2}). We reiterate that the notable efficiency improvements over 25% are not attributable to defect reduction.

Built-in potential analysis at 3D/SIG-2D junction

What is clear, however, is the greater observed reduction in non-radiative recombination within the 3D/SIG-Br device than within the SIG-I device, which can again be proven by the improvements in electroluminescence quantum efficiency (ELQE) (Fig. 4a).¹⁷ The ELQE value, when the current density was injected into a device as much as *J*_{SC} under standard test conditions of solar cells, directly correlates with the *V*_{OC} of the solar cell. These ELQE values were derived to be 0.14, 3.62, and 9.63% for the 3D, 3D/SIG-I, and 3D/SIG-Br devices, respectively. We therefore hypothesized that the observed difference between SIG-I and SIG-Br is attributable to variations related to *V*_{bi}, rather than to defects. A notable distinction upon introducing SIG-2D is the alteration in *V*_{bi}, as deduced from the reliable Mott–Schottky plot conducted for each of the PSCs (Fig. 4b).⁵⁰ The 3D device exhibited a *V*_{bi} of 1.081 V, whereas the introduction of the SIG-I and SIG-Br layers increased the *V*_{bi} to 1.150 V and 1.207 V, respectively. This increase in *V*_{bi} was similarly seen in devices without HTL (Fig. S12, ESI†). In the context of the 3D/SIG-2D junction, where each layer is postulated to function as a distinct semiconductor, this shift in *V*_{bi} can be attributed to the ϕ to each 2D layer. At the same time, we can map the spatial distributions of defect densities in our devices using Mott–Schottky plots (Fig. 4c). We observed no significant differences in the defect densities (*N*) at interfaces near the ETL in our devices (3D device: 3.52×10^{16} cm^{−3}, 3D/SIG-I device: 3.55×10^{16} cm^{−3}, 3D/SIG-Br device: 3.55×10^{16} cm^{−3}). Conversely, the introduction of SIG-2D was found to decrease *N* at the HTL interface (3D device: 1.92×10^{16} cm^{−3}, 3D/SIG-I device: 1.24×10^{16} cm^{−3}, 3D/SIG-Br device: 1.03×10^{16} cm^{−3}). Reducing the defects will certainly improve *V*_{OC} and FF; however, the enhancements observed in *V*_{OC} and FF were greater than expected.⁵¹

The energy levels including local electrical field and discontinuity in the band structure within a device significantly influence its efficiency and stability.^{52,53} As such, we have observed changes in the internal energy levels according to

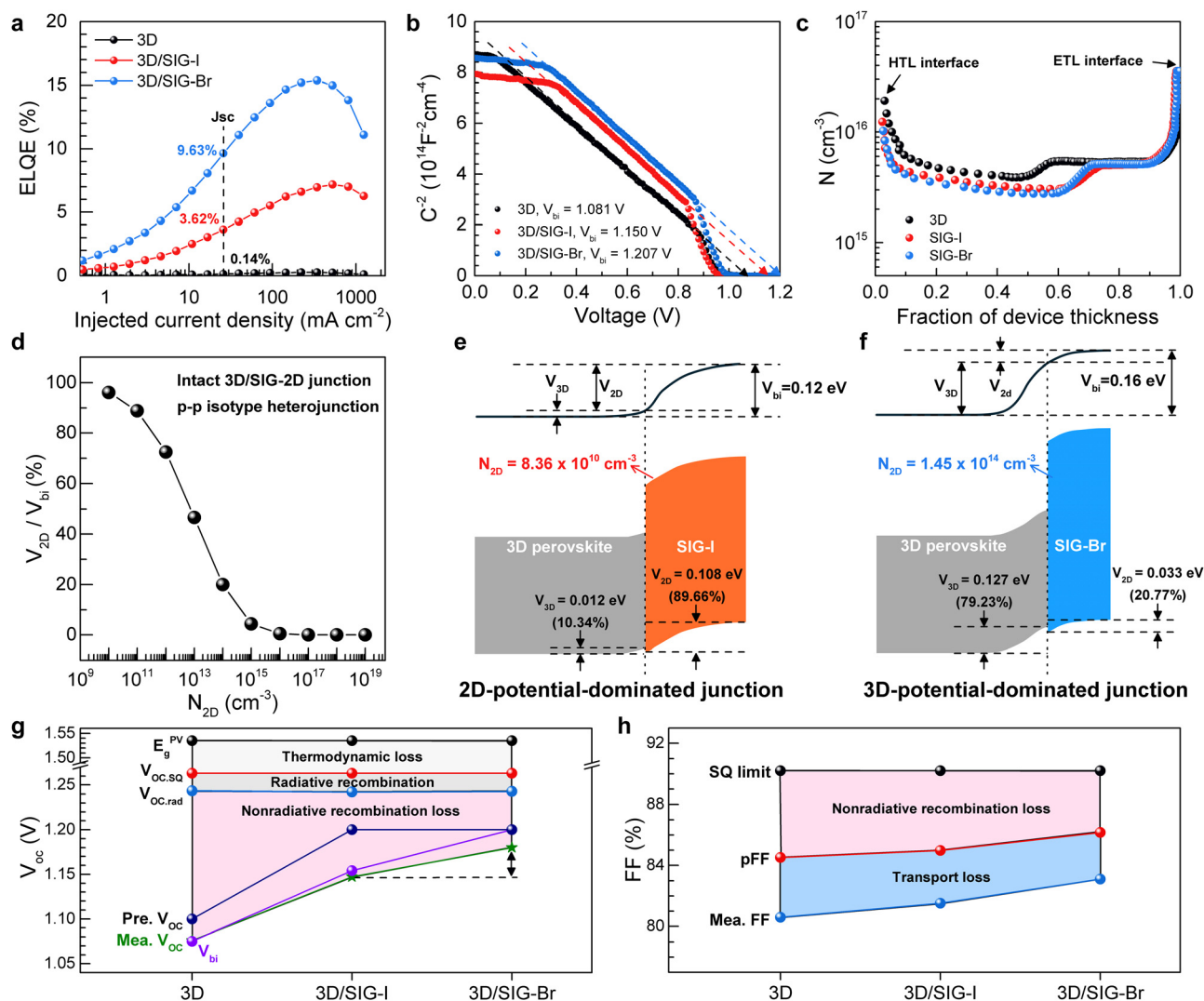


Fig. 4 Photovoltaic performance and characterization of the devices: (a) ELQE of our device according to the injected current density. (b) Mott-Schottky plots of the 3D, 3D/SIG-I, and 3D/SIG-Br devices with FTO/SnO₂/3D/(SIG-2D)/Spiro-OMeTAD/Au structure. (c) DLCP analysis for 3D, 3D/SIG-I, and 3D/SIG-Br devices with full structure. (d) Ratio of V_{2D}/V_{3D} according to N_{2D} in p-p isotype heterojunction. (e) Distribution of V_{bi} in the 3D/SIG-I junction for $N_{2D} = 7.93 \times 10^{10} \text{ cm}^{-3}$. (f) Distribution of V_{bi} in the 3D/SIG-Br junction for $N_{2D} = 1.45 \times 10^{14} \text{ cm}^{-3}$. (g) Detailed V_{oc} loss analysis and (h) FF loss analysis of the 3D, 3D/SIG-I, and 3D/SIG-Br devices. In panels E and F, the values of V_{bi} for the 3D/SIG-I and 3D/SIG-Br heterojunctions were determined based on the ΔE_{vac} identified through UPS measurement.

the introduction of an SIG-Br layer. For this purpose, the energy level of the 3D thin film was initially characterized. The ϕ of 3D FAPbI₃ was determined as 4.82 eV, aligned with previous findings (Fig. S13, ESI†).^{54,55} Prior to forming the 3D/SIG-2D junction, it was found that the ϕ values of (BA)₂PbI₄ and (BA)₂PbBr₄ are deeper by 0.12 eV and 0.34 eV, respectively, than that of 3D perovskite. The change in the ϕ after forming the 3D/SIG-2D junction provides insights into the local electrical field generated at these junctions. We have additionally observed these changes using UPS and KPFM (Fig. S14 and S15, ESI†). For the 3D/SIG-I junction, the work function increased by 0.12 eV compared to the standalone 3D perovskite. Substituting SIG-Br for SIG-I resulted in a further deepening in the work function by 40 meV. These results indicate that replacing the SIG-2D layer with SIG-Br leads to a larger shift in the vacuum

level. Although these energy levels do not exactly match those of the original 2D perovskite film, we believe that the local electrical field induced by this vacuum level shift can be attributed to the inherent differences in the energy levels of the initial 2D perovskite. Furthermore, we investigated the aligned VBM values after achieving equilibrium in 3D and SIG-2D perovskite heterojunctions, meaning after Fermi-level alignment (Table S5, ESI†). Aligned VBMs were found to be −5.43 eV for the SIG-I layer and −5.31 eV for the SIG-Br layer. These levels are slightly shallower than the −5.53 eV of the 3D perovskite, which is not expected to negatively impact charge transport in a photovoltaic device.

Since it was confirmed that the 3D and SIG-2D layers are compositionally independent and each is a p-type semiconductor, the 3D/SIG-2D bilayer forms a p-p isotype heterojunction,

which induces a positive V_{bi} according to Anderson's rule. Although using 2D with deep ϕ achieved through Br substitution always enhances the internal electric field, understanding the V_{bi} formation process in p-p isotype heterojunctions is essential for optimizing their utilization. In the p-p isotype heterojunction, the V_{bi} formation process can be categorized into two phases, depending on whether the thickness of 2D exceeds the depletion width (critical thickness) or not, as illustrated in Fig. S16 (ESI†): (i) a fully depleted 2D region when the thickness of 2D is under the depletion width and (ii) a partially depleted 2D region when thickness of the 2D layer is thicker than the depletion width. In a fully depleted 2D region, as the thickness of the SIG-2D layer progressively increases on top of the 3D layer, the V_{bi} correspondingly increases. The 2D induced V_{bi} increases until the thickness reaches the 'critical thickness', where V_{bi} matches the difference between the ϕ of the two semiconductors ($V_{bi} = \phi_{3D} - \phi_{2D}$). However, surpassing this critical thickness leads to a partially depleted junction, where V_{bi} remains unchanged regardless of any further increase in thickness. In this region, any excess SIG-2D that does not contribute to V_{bi} can introduce resistance due to the low conductivity of the 2D layer. In practice, the W_{2D} of the SIG-Br layer formed under each condition according to SIG process temperature (30, 45, and 60 degrees celsius) was verified (Fig. S17, ESI†). The maximum thickness of the SIG-Br layer was 40.1 nm at 60 degrees celsius. Above this temperature, quasi-2D perovskite forms instead of the desired pure 2D perovskite, deviating from the intended 3D/pure 2D structure design (Fig. S6, ESI†). As the thickness of the 2D layer increases from 26.5 nm to 40.1 nm, the V_{OC} and FF of the solar cell also increase, resulting in a PCE of over 25% (Fig. S18, ESI†). In addition to the increase in V_{OC} , the enhancement in V_{bi} observed with increasing thickness of W_{2D} suggests that the SIG-Br layer has not exceeded its critical thickness (Fig. S19, ESI†). These results indicate that if SIG-Br layers thicker than 40.1 nm can be produced, solar cells might achieve performance levels surpassing the current 25.47%. Unfortunately, the only feasible method to achieve additional W_{2D} in the SIG-Br layer is to enhance the repeatability of the process, since increasing the process temperature is not an option. The solar cells produced through this iteration of the process exhibited a slight improvement in V_{bi} ; however, an overall enhancement in performance was not realized due to a reduction in FF (Fig. S20 and S21, ESI†).

Even when the characteristics of both semiconductors in the isotype heterojunction are defined, such as a p-p junction, discussing and quantifying their properties as in an anisotype junction is not straightforward.⁵⁶ One approach to interpreting such isotype heterojunctions involves utilizing the continuity of electric displacement.⁵⁷ By utilizing this continuity and quantifying the concentration of each heterogeneous material along with the formed V_{bi} , it is possible to derive information about the distribution of V_{bi} at the junction (Note S1, ESI†). As shown in Fig. 4d, the V_{bi} across the 3D region (V_{3D}) and V_{bi} formed in the 2D region (V_{2D}) were calculated according to the 2D concentration (N_{2D}). When N_{2D} is 10^{10} cm^{-3} , 95% of V_{bi} is

applied across the 2D region. However, as the concentration of N_{2D} continuously increases, there is a corresponding decrease in V_{2D} . Once N_{2D} reaches the point 10^{19} cm^{-3} , all of V_{bi} exists within the 3D region. Importantly, the total V_{bi} remains constant throughout this process. These results suggest that, although the structural designs of the 3D/SIG-I and 3D/SIG-Br junctions are the same, being p-p isotype heterojunctions, the specific internal electric fields designed within the devices may have distinct electric field structures. To apply this interpretation, it is necessary to define the concentration of the 2D layer. Therefore, we have derived the N_{2D} from the results of UPS (Note S2, ESI†). N_{2D} of $(\text{BA})_2\text{PbI}_4$ and $(\text{BA})_2\text{PbBr}_4$ were determined to be $8.36 \times 10^{10} \text{ cm}^{-3}$ and $1.45 \times 10^{14} \text{ cm}^{-3}$, respectively. For the 3D/SIG-I junction, V_{2D} was calculated to be 0.108 eV, indicating that 89.66% of the total V_{bi} (0.12 eV) was formed in the SIG-2D region (Fig. 4e). These 2D-potential-dominated junctions are consistent with our previous predictions. In contrast, for the 3D/SIG-Br junction, it transitions to a 3D-potential-dominated junction, with 79.23% of the total V_{bi} (0.16 eV) occurring within the 3D perovskite region (Fig. 4f). These changes clearly indicate a shift in the energy profiling within the 3D/SIG-2D junction. These results imply that 2D perovskites with a deep ϕ can increase V_{bi} , which can positively affect effective charge extraction and enhance charge transport under short-circuit conditions.^{58,59} Additionally, the N_{2D} of the 2D perovskite can alter the distribution of V_{bi} within the device.⁵⁷

To compare and analyze the effects between the 3D/SIG-I and 3D/SIG-Br junctions, we consolidated and plotted information related to V_{OC} in Fig. 4g. The photovoltaic bandgap (E_g^{PV}) for each condition was calculated to be 1.535 eV using the EQE spectrum (Fig. S22, ESI†).⁶⁰ Since no variations in the external quantum efficiency (EQE) were observed based on the variable, neither the open-circuit voltage in the Shockley–Queisser limit ($V_{OC,\text{SQ}}$) at 1.263 eV nor in the radiative limit ($V_{OC,\text{rad}}$) at 1.243 eV exhibited any changes. The V_{OC} anticipated from the lifetime observed in the above TRPL (Pre. V_{OC}), exhibits a consistent value of 1.2 V with the insertion of SIG-2D. However, unlike the behavior of Pre. V_{OC} , we confirmed that the variations in the actually measured V_{OC} (Mea. V_{OC}) align more closely with the changes in the built-in potential. This suggests that the efficiency realized with SIG-Br is not solely attributable to defect minimization. The 33 mV increase in V_{OC} , observed when compared to SIG-I, is derived from the 40 meV difference in ϕ between SIG-I and SIG-Br layers. Although a thicker SIG-2D layer—compared to those typically obtained through solution processes—can enhance the internal electric field, it may also impede the transport of photoexcited charges. To quantitatively analyze the transport loss, we monitored the J - V curve at various light intensities and calculated the pseudo-FF (pFF) from the pseudo- J - V curve, where charge transport loss is disregarded (Fig. 4h and Fig. S23, ESI†). The incorporation of thick SIG-I and SIG-Br layers did not lead to additional transport loss, a phenomenon evidenced by the disparity between pFF and the measured FF (Mea. FF). This can likely be attributed to transport acceleration induced by the local electric field effect.

Stability test according to 3D/SIG-2D junction

Fig. 5a displays the storage stability of the encapsulated PV device with 3D/SIG-Br, which exhibits an initial efficiency of 25%. During this period, samples were sent to the Solar Energy Research Institute of Singapore (SERIS) for cross-verification of the device performance, confirming the certified efficiency of 25.4% (Fig. S24, ESI†). Upon the sample's return, periodic measurements were conducted, with 97% of the initial efficiency retained after 456 hours (Fig. S25 and Table S6, ESI†). The photostability of the encapsulated devices was assessed under continuous illumination (Fig. 5b). Using maximum power point tracking (MPPT), the 3D device retained 88% of its stabilized efficiency (PCE = 22.09%) after 256 hours. More specifically, when evaluating the device stability, a stabilized time to 90% (T_{S90}) of 118 hours was obtained for the 3D device. The introduction of SIG-Br was found to enhance stability under MPPT conditions, maintaining 89% of the stabilized efficiency (PCE = 25.29%) after 770 hours. This improvement in operational stability is speculated to result from enhancements in the internal field design and energy levels.⁵² In addition to storage stability and operational stability, monitoring the stability of solar cells at 85 degrees Celsius is another crucial evaluation indicator (Fig. 5c). Unfortunately, Spiro-OMeTAD, a component of our device, is a significant factor that impedes the evaluation of thermal stability. Therefore, to monitor the thermal stability of

3D/SIG-2D, we replaced the HTL with Li-free poly(triarylamine) (PTAA). After 12 hours, the efficiency of the 3D/SIG-I devices improved to an average of 21%, and the 3D/SIG-Br devices reached 22%, in contrast to the 16% efficiency observed in the control device. The 3D device maintained 83% of its steady-state efficiency after 200 hours, whereas the 3D/SIG-2D devices demonstrated efficiency retentions of 91% and 92%, respectively, over the same period (Fig. S26, ESI†). The efficiency reduction issue may be attributed to junction breakdown and changes in the light absorption layer caused by deprotonation.⁶¹ When analyzing the PV parameters of the highest efficiency cell in each condition over time, we observed a decline in V_{OC} and FF (Table S7, ESI†). These results indicate that the formation of intact 3D/SIG-2D junctions contributes not only to efficiency improvements but also to enhanced thermal stability. Although the difference is modest, of approximately 1%, our analysis of the 2D materials itself reveals an improvement in thermal durability for $(BA)_2PbBr_4$ compared to $(BA)_2PbI_4$ (Fig. S26, ESI†). This result is predicted to have affected the thermal stability of the devices we derived.

Conclusions

Here, in the design of 3D/2D junctions, we demonstrate that deeper work function levels in the 2D layer enhances the

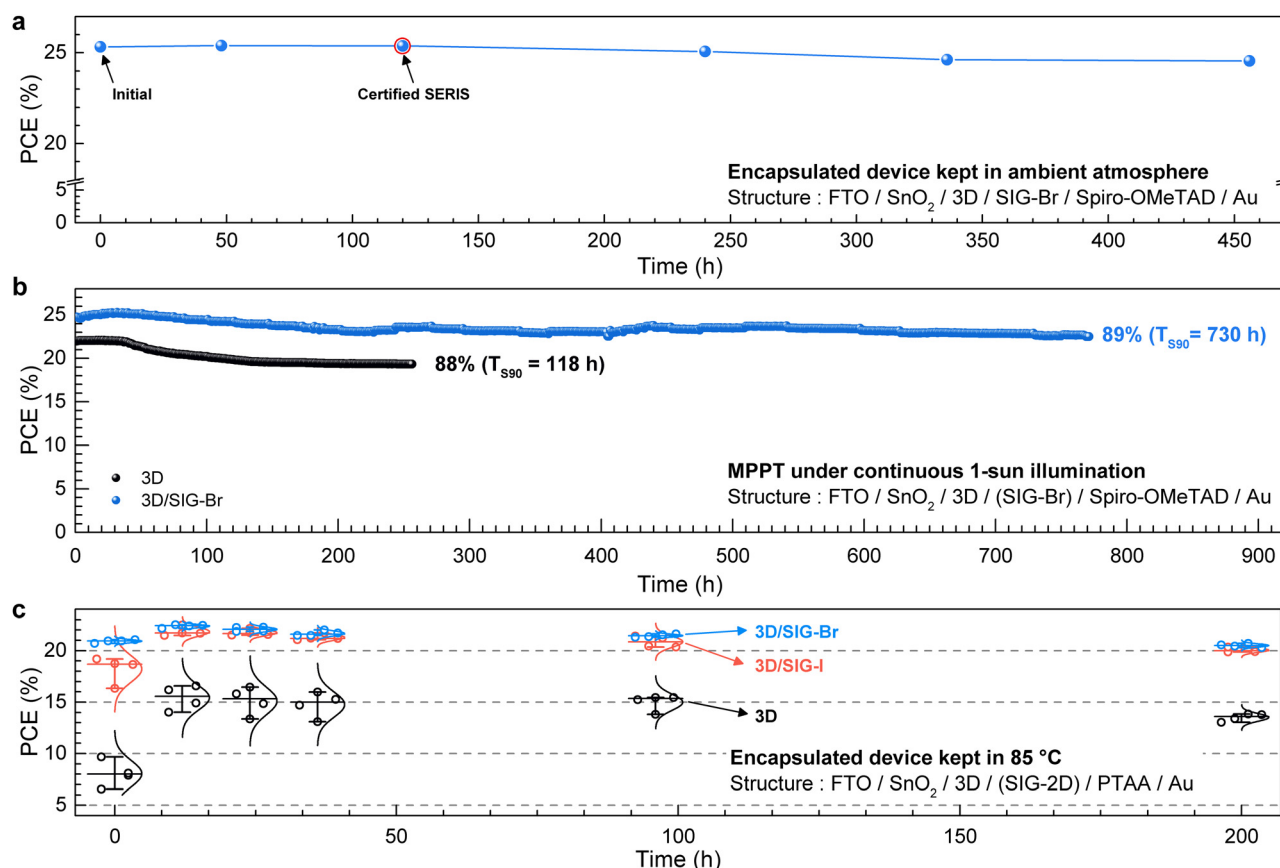


Fig. 5 Stability tests for 3D/SIG-Br device: (a) storage stability performance of 3D/SIG-Br device. (b) Long-term operational stability test of encapsulated devices at the maximum power point. (c) The thermal stability of the 3D, 3D/SIG-I and 3D/SIG-Br devices at 85 °C.

internal built-in potential, as evidenced by comparing intact 3D/SIG-I and 3D/SIG-Br bilayers. Stacking (BA)₂PbBr₄ onto a 3D perovskite layer, we achieved a 3D/SIG-Br bilayer with an enhanced built-in potential, yielding a maximum PCE of 25.47% (certified at 25.37%). Although not as optimized as (BA)₂PbBr₄, we have observed that 2D perovskites made from 4-fluoro-phenethylammonium lead iodide, which exhibit deeper work functions, can also achieve improved open-circuit voltages to 1.182 V of V_{OC} (Fig. S28, ESI†). Devices with these 3D/SIG-Br junctions maintain operational stability for 700 hours despite an unbalanced halide distribution, and their thermal stability has been verified for 200 hours at 85 degrees Celsius. Our findings extend beyond mere defect control through 2D formation; they uncover additional design factors, such as work function and internal field distribution, and provide guidance for more effective 3D/2D device design.

Author contributions

S. L. and H. C. contributed equally to this work. S. L., H. C. and J. H. N. conceived the work and designed the experiment. S. L., H. C., O. J. O., and D. H. K. fabricated and characterized the perovskite thin films and device under different conditions. O. J. O. performed KPFM to verify the energy levels of the perovskite during the revision process. D. H. K. performed capacitance-voltage measurements of the perovskite solar cells during the revision process. J. H. N. directed and supervised this project. All authors discussed the results and contributed to the writing of the paper.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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References

- 1 J. Jeong, M. Kim, J. Seo, H. Lu, P. Ahlawat, A. Mishra, Y. Yang, M. A. Hope, F. T. Eickemeyer, M. Kim, Y. J. Yoon, I. W. Choi, B. P. Darwich, S. J. Choi, Y. Jo, J. H. Lee, B. Walker, S. M. Zakeeruddin, L. Emsley, U. Rothlisberger, A. Hagfeldt, D. S. Kim, M. Grätzel and J. Y. Kim, *Nature*, 2021, **592**, 381–385.
- 2 G. Li, Z. Su, L. Canil, D. Hughes, M. H. Aldamasy, J. Dagar, S. Trofimov, L. Wang, W. Zuo, J. J. Jerónimo-Rendon, M. M. Byranvand, C. Wang, R. Zhu, Z. Zhang, F. Yang, G. Nasti, B. Naydenov, W. C. Tsoi, Z. Li, X. Gao, Z. Wang, Y. Jia, E. Unger, M. Saliba, M. Li and A. Abate, *Science*, 2023, **379**, 399–403.
- 3 M. J. Jeong, C. S. Moon, S. Lee, J. M. Im, M. Y. Woo, J. H. Lee, H. Cho, S. W. Jeon and J. H. Noh, *Joule*, 2023, **7**, 112–127.
- 4 Z. Yu, Z. Yang, Z. Ni, Y. Shao, B. Chen, Y. Lin, H. Wei, Z. J. Yu, Z. Holman and J. Huang, *Nat. Energy*, 2020, **5**, 657–665.
- 5 W. Peng, K. Mao, F. Cai, H. Meng, Z. Zhu, T. Li, S. Yuan, Z. Xu, X. Feng, J. Xu, M. D. McGehee and J. Xu, *Science*, 2023, **379**, 683–690.
- 6 W. Chen, S. Liu, Q. Li, Q. Cheng, B. He, Z. Hu, Y. Shen, H. Chen, G. Xu, X. Ou, H. Yang, J. Xi, Y. Li and Y. Li, *Adv. Mater.*, 2022, **34**, 2110482.
- 7 S. Moon, K. Kim, Y. Kim, J. Heo and J. Lee, *Sci. Rep.*, 2016, **6**, 30107.
- 8 W. Metaferia, K. L. Schulte, J. Simon, S. Johnston and A. J. Ptak, *Nat. Commun.*, 2019, **10**, 3361.
- 9 H.-C. Fu, W. Li, Y. Yang, C.-H. Lin, A. Veyssal, J.-H. He and S. Jin, *Nat. Commun.*, 2021, **12**, 156.
- 10 X. Qu, Y. He, M. Qu, T. Ruan, F. Chu, Z. Zheng, Y. Ma, Y. Chen, X. Ru, X. Xu, H. Yan, L. Wang, Y. Zhang, X. Hao, Z. Hameiri, Z.-G. Chen, L. Wang and K. Zheng, *Nat. Energy*, 2021, **6**, 194–202.
- 11 K. Yoshikawa, H. Kawasaki, W. Yoshida, T. Irie, K. Konishi, K. Nakano, T. Uto, D. Adachi, M. Kanematsu, H. Uzu and K. Yamamoto, *Nat. Energy*, 2017, **2**, 17032.
- 12 H. Lin, M. Yang, X. Ru, G. Wang, S. Yin, F. Peng, C. Hong, M. Qu, J. Lu, L. Fang, C. Han, P. Procel, O. Isabella, P. Gao, Z. Li and X. Xu, *Nat. Energy*, 2023, **8**, 789–799.
- 13 Best research-cell efficiency chart, <https://www.nrel.gov/pv/cell-efficiency.html>.
- 14 P. Shi, Y. Ding, B. Ding, Q. Xing, T. Kodalle, C. M. Sutter-Fella, I. Yavuz, C. Yao, W. Fan, J. Xu, Y. Tian, D. Gu, K. Zhao, S. Tan, X. Zhang, L. Yao, P. J. Dyson, J. L. Slack, D. Yang, J. Xue, M. K. Nazeeruddin, Y. Yang and R. Wang, *Nature*, 2023, **620**, 323–327.
- 15 J. Park, J. Kim, H.-S. Yun, M. J. Paik, E. Noh, H. J. Mun, M. G. Kim, T. J. Shin and S. I. Seok, *Nature*, 2023, **616**, 724–730.
- 16 Y. Zhang, Y. Li, L. Zhang, H. Hu, Z. Tang, B. Xu and N.-G. Park, *Adv. Energy Mater.*, 2021, **11**, 2102538.
- 17 C. Cho, Y.-W. Jang, S. Lee, Y. Vaynzof, M. Choi, J. H. Noh and K. Leo, *Sci. Adv.*, 2021, **7**, eabj1363.
- 18 J. Xia, C. Liang, H. Gu, S. Mei, Y. Cai and G. Xing, *ACS Appl. Electron. Mater.*, 2022, **4**, 1939–1948.
- 19 P. Cui, D. Wei, J. Ji, H. Huang, E. Jia, S. Dou, T. Wang, W. Wang and M. Li, *Nat. Energy*, 2019, **4**, 150–159.

- 20 R. Ji, Z. Zhang, Y. J. Hofstetter, R. Buschbeck, C. Hänisch, F. Paulus and Y. Vaynzof, *Nat. Energy*, 2022, **7**, 1170–1179.
- 21 S. S. Mali, J. V. Patil, J.-Y. Shao, Y.-W. Zhong, S. R. Rondiya, N. Y. Dzade and C. K. Hong, *Nat. Energy*, 2023, **8**, 989–1001.
- 22 X. Lian, H. Zhang, X. Mo and J. Chu, *Commun. Chem.*, 2023, **6**, 11.
- 23 H. Li, C. Zhang, C. Gong, D. Zhang, H. Zhang, Q. Zhuang, X. Yu, S. Gong, X. Chen, J. Yang, X. Li, R. Li, J. Li, J. Zhou, H. Yang, Q. Lin, J. Chu, M. Grätzel, J. Chen and Z. Zang, *Nat. Energy*, 2023, **8**, 946–955.
- 24 S. Ye, H. Rao, M. Feng, L. Xi, Z. Yen, D. H. L. Seng, Q. Xu, C. Boothroyd, B. Chen, Y. Guo, B. Wang, T. Salim, Q. Zhang, H. He, Y. Wang, X. Xiao, Y. M. Lam and T. C. Sum, *Nat. Energy*, 2023, **8**, 284–293.
- 25 E. Shi, B. Yuan, S. B. Shiring, Y. Gao, Akriti, Y. Guo, C. Su, M. Lai, P. Yang, J. Kong, B. M. Savoie, Y. Yu and L. Dou, *Nature*, 2020, **580**, 614–620.
- 26 Y. Liu, S. Akin, L. Pan, R. Uchida, N. Arora, J. V. Milić, A. Hinderhofer, F. Schreiber, A. R. Uhl, S. M. Zakeeruddin, A. Hagfeldt, M. I. Dar and M. Grätzel, *Sci. Adv.*, 2019, **5**, eaaw2543.
- 27 J. J. Yoo, S. Wiegbold, M. C. Sponseller, M. R. Chua, S. N. Bertram, N. T. P. Hartono, J. S. Tresback, E. C. Hansen, J.-P. Correa-Baena and V. Bulović, *Energy Environ. Sci.*, 2019, **12**, 2192–2199.
- 28 E. Jokar, P.-Y. Cheng, C.-Y. Lin, S. Narra, S. Shahbazi and E. Wei-Guang Diao, *ACS Energy Lett.*, 2021, **6**, 485–492.
- 29 F. Wang, X. Jiang, H. Chen, Y. Shang, H. Liu, J. Wei, W. Zhou, H. He, W. Liu and Z. Ning, *Joule*, 2018, **2**, 2732–2743.
- 30 Y. Cho, A. M. Soufiani, J. S. Yun, J. Kim, D. S. Lee, J. Seidel, X. Deng, M. A. Green, S. Huang and A. W. Y. Ho-Baillie, *Adv. Energy Mater.*, 2018, **8**, 1703392.
- 31 J. Lu, L. Jiang, W. Li, F. Li, N. K. Pai, A. D. Scully, C.-M. Tsai, U. Bach, A. N. Simonov, Y.-B. Cheng and L. Spiccia, *Adv. Energy Mater.*, 2017, **7**, 1700444.
- 32 L. N. Quan, M. Yuan, R. Comin, O. Voznyy, E. M. Beauregard, S. Hoogland, A. Buin, A. R. Kirmani, K. Zhao, A. Amassian, D. H. Kim and E. H. Sargent, *J. Am. Chem. Soc.*, 2016, **138**, 2649–2655.
- 33 S. Sidhik, Y. Wang, M. De Siena, R. Asadpour, A. J. Torma, T. Terlier, K. Ho, W. Li, A. B. Puthirath, X. Shuai, A. Agrawal, B. Traore, M. Jones, R. Giridharagopal, P. M. Ajayan, J. Strzalka, D. S. Ginger, C. Katan, M. A. Alam, J. Even, M. G. Kanatzidis and A. D. Mohite, *Science*, 2022, **377**, 1425–1430.
- 34 Y.-W. Jang, S. Lee, K. M. Yeom, K. Jeong, K. Choi, M. Choi and J. H. Noh, *Nat. Energy*, 2021, **6**, 63–71.
- 35 R. K. Purohit and B. L. Sharma, *Semiconductor heterojunctions*, Elsevier, Amsterdam, 2015.
- 36 S. Silver, J. Yin, H. Li, J.-L. Brédas and A. Kahn, *Adv. Energy Mater.*, 2018, **8**, 1703468.
- 37 E. S. Vasileiadou, I. Hadar, M. Kepenekian, J. Even, Q. Tu, C. D. Malliakas, D. Friedrich, I. Spanopoulos, J. M. Hoffman, V. P. Dravid and M. G. Kanatzidis, *Chem. Mater.*, 2021, **33**, 5085–5107.
- 38 F. Zhang, F. Ullrich, S. Silver, R. A. Kerner, B. P. Rand and A. Kahn, *J. Phys. Chem. Lett.*, 2019, **10**, 890–896.
- 39 E. Choi, Y. Zhang, A. M. Soufiani, M. Lee, R. F. Webster, M. E. Pollard, P. J. Reece, W. Lee, J. Seidel, J. Lim, J.-H. Yun and J. S. Yun, *npj 2D Mater. Appl.*, 2022, **6**, 43.
- 40 R. Lin, Y. Wang, Q. Lu, B. Tang, J. Li, H. Gao, Y. Gao, H. Li, C. Ding and J. Wen, *Nature*, 2023, **620**, 994–1000.
- 41 J. Xue, R. Wang and Y. Yang, *Nat. Rev. Mater.*, 2020, **5**, 809–827.
- 42 S. Ning, S. Zhang, J. Sun, C. Li, J. Zheng, Y. Khalifa, S. Zhou, J. Cao and Y. Wu, *ACS Appl. Mater. Interfaces*, 2020, **12**, 43705–43713.
- 43 W.-C. Lin, W.-C. Lo, J.-X. Li, Y.-K. Wang, J.-F. Tang and Z.-Y. Fong, *npj Mater. Degrad.*, 2021, **5**, 13.
- 44 J. Hu, R. A. Kerner, I. Pelczer, B. P. Rand and J. Schwartz, *ACS Energy Lett.*, 2021, **6**, 2262–2267.
- 45 T. Kirchartz, J. A. Márquez, M. Stolterfoht and T. Unold, *Adv. Energy Mater.*, 2020, **10**, 1904134.
- 46 B. Zhao, S. Bai, V. Kim, R. Lamboll, R. Shivanna, F. Auras, J. M. Richter, L. Yang, L. Dai, M. Alsari, X.-J. She, L. Liang, J. Zhang, S. Lilliu, P. Gao, H. J. Snaith, J. Wang, N. C. Greenham, R. H. Friend and D. Di, *Nat. Photonics*, 2018, **12**, 783–789.
- 47 M. Stolterfoht, C. M. Wolff, J. A. Márquez, S. Zhang, C. J. Hages, D. Rothhardt, S. Albrecht, P. L. Burn, P. Meredith, T. Unold and D. Neher, *Nat. Energy*, 2018, **3**, 847–854.
- 48 Q. Jiang, Y. Zhao, X. Zhang, X. Yang, Y. Chen, Z. Chu, Q. Ye, X. Li, Z. Yin and J. You, *Nat. Photonics*, 2019, **13**, 460–466.
- 49 A. A. Sutanto, P. Caprioglio, N. Drigo, Y. J. Hofstetter, I. Garcia-Benito, V. I. Queloz, D. Neher, M. K. Nazeeruddin, M. Stolterfoht and Y. Vaynzof, *Chem*, 2021, **7**, 1903–1916.
- 50 M. Fischer, K. Tvingstedt, A. Baumann and V. Dyakonov, *ACS Appl. Energy Mater.*, 2018, **1**, 5129–5134.
- 51 A. S. Chouhan, N. P. Jasti and S. Avasthi, *Mater. Lett.*, 2018, **221**, 150–153.
- 52 S. Tan, T. Huang, I. Yavuz, R. Wang, T. W. Yoon, M. Xu, Q. Xing, K. Park, D.-K. Lee and C.-H. Chen, *Nature*, 2022, **605**, 268–273.
- 53 W. Yang, B. Ding, Z. Lin, J. Sun, Y. Meng, Y. Ding, J. Sheng, Z. Yang, J. Ye and P. J. Dyson, *Adv. Mater.*, 2023, **35**, 2302071.
- 54 Q. Jiang, J. Tong, Y. Xian, R. A. Kerner, S. P. Dunfield, C. Xiao, R. A. Scheidt, D. Kuciauskas, X. Wang, M. P. Hautzinger, R. Tirawat, M. C. Beard, D. P. Fenning, J. J. Berry, B. W. Larson, Y. Yan and K. Zhu, *Nature*, 2022, **611**, 278–283.
- 55 S. Tan, T. Huang, I. Yavuz, R. Wang, T. W. Yoon, M. Xu, Q. Xing, K. Park, D.-K. Lee, C.-H. Chen, R. Zheng, T. Yoon, Y. Zhao, H.-C. Wang, D. Meng, J. Xue, Y. J. Song, X. Pan, N.-G. Park, J.-W. Lee and Y. Yang, *Nature*, 2022, **605**, 268–273.
- 56 B. Sharma and R. Purohit, *Semiconductor heterojunctions*, Elsevier, 2015.
- 57 R. L. Anderson, *Solid-State Electron.*, 1962, **5**, 341–351.
- 58 T. Kirchartz, J. Bisquert, I. Mora-Sero and G. Garcia-Belmonte, *Phys. Chem. Chem. Phys.*, 2015, **17**, 4007–4014.
- 59 U. Rau and T. Kirchartz, *Adv. Mater. Interfaces*, 2019, **6**, 1900252.
- 60 P. K. Nayak, S. Mahesh, H. J. Snaith and D. Cahen, *Nat. Rev. Mater.*, 2019, **4**, 269–285.
- 61 M. Wang, Z. Shi, C. Fei, Z. J. D. Deng, G. Yang, S. P. Dunfield, D. P. Fenning and J. Huang, *Nat. Energy*, 2023, **8**, 1229–1239.