# Perovskite superlattices with efficient carrier dynamics

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Compared with their three-dimensional (3D) counterparts, low-dimensional metal halide perovskites (2D and quasi-2D;  $B_2A_{n-1}M_nX_{3n+1}$ , such as  $B = R-NH_3^+$ ,  $A = HC(NH_2)_2^+$ ,  $Cs^+$ ; M = Pb<sup>2+</sup>, Sn<sup>2+</sup>; X = Cl<sup>-</sup>, Br<sup>-</sup>, l<sup>-</sup>) with periodic inorganic-organic structures have shown promising stability and hysteresis-free electrical performance<sup>1-6</sup>. However, their unique multiple-quantum-well structure limits the device efficiencies because of the grain boundaries and randomly oriented quantum wells in polycrystals<sup>7</sup>. In single crystals, the carrier transport through the thickness direction is hindered by the layered insulating organic spacers<sup>8</sup>. Furthermore, the strong quantum confinement from the organic spacers limits the generation and transport of free carriers<sup>9,10</sup>. Also, lead-free metal halide perovskites have been developed but their device performance is limited by their low crystallinity and structural instability<sup>11</sup>. Here we report a low-dimensional metal halide perovskite  $BA_2MA_{n-1}Sn_nI_{3n+1}$  (BA, butylammonium; MA, methylammonium; n = 1, 3, 5) superlattice by chemical epitaxy. The inorganic slabs are aligned vertical to the substrate and interconnected in a criss-cross 2D network parallel to the substrate, leading to efficient carrier transport in three dimensions. A lattice-mismatched substrate compresses the organic spacers, which weakens the quantum confinement. The performance of a superlattice solar cell has been certified under the quasi-steady state, showing a stable 12.36% photoelectric conversion efficiency. Moreover, an intraband exciton relaxation process may have yielded an unusually high open-circuit voltage ( $V_{0C}$ ).

We studied the growth process and structure of BA<sub>2</sub>SnI<sub>4</sub> (n = 1) superlattice on a MAPb<sub>0.5</sub>Sn<sub>0.5</sub>Br<sub>3</sub> substrate (Supplementary Discussion 1 and Supplementary Figs. 1-4). The Sn-I slabs exhibit a favourable epitaxial relationship with the substrate, forming a thermodynamically stable, vertically aligned lattice<sup>12</sup> (Supplementary Fig. 1). Scanning electron microscopy (SEM) images show that the crystals first grow into criss-cross vertical thin plates followed by lateral merging (Fig. 1a and Supplementary Fig. 2). Similar growth behaviour can be observed in other low-dimensional perovskites grown on different substrates (Supplementary Figs. 3 and 5). Cryogenic scanning transmission electron microscopy (STEM) was used to study the structure of a single plate, which exhibits anisotropy (Fig. 1b). The a-c plane shows a periodic distribution of inorganic Sn-I slabs and organic BA spacers along the a direction (Fig. 1b, middle and Supplementary Fig. 6). The b-c plane shows a continuous Sn-I slab with a coherent heteroepitaxial interface with the substrate (Fig. 1b, right). Therefore, the criss-cross vertical plates on the substrates create a 3D network of Sn-I slabs, not seen previously in any polycrystals (Supplementary Fig. 7) or conventionally grown single crystals. Furthermore, grazing-incidence wide-angle X-ray scattering further verified their vertically aligned structures<sup>13,14</sup> (Supplementary Fig. 8).

To further study the crystal orientation in the a-b plane, we measured the polarization-dependent photocurrent of superlattices and conventionally grown single crystals (Fig. 1c). The results in both show a strong dependence on the polarization direction, but the response of superlattices has a 90° period, whereas that of conventionally grown single crystals has a 180° period. This is because the inorganic slabs are aligned in two perpendicular orientations in the a-b plane of superlattices, but in only one orientation of conventionally grown single crystals (Supplementary Fig. 9). Similar trends can also be observed in the carrier lifetime obtained from orientation-dependent transient photovoltage measurements (Fig. 1d and Supplementary Fig. 10). These results collectively support that the superlattice has Sn-I slabs interconnected, with numerous criss-cross thin plates merged in the a-b plane.

Because of the interconnected Sn-I slabs, carriers in the superlattice do not need to cross any grain boundaries or organic spacers both in plane and out of plane. Transient photocurrent measurements along

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0

0

45 Rotation angle (°)

90

Fig. 1 | Structural characterizations of the BA2SNI4 superlattice. a, SEMtheimages showing the criss-cross epitaxial BA2SNI4 superlattice before andsubafter merging into a thin film. Scale bars,  $2 \, \mu$ m. b, Schematic (left) anddiffatomic-resolution cryogenic STEM images (middle and right) showing thepolsuperlattice structure of a single plate. Cryogenic STEM is essential to(to)minimize the damage of beam-sensitive materials. The epitaxial layer has acrywell-aligned anisotropic structure without grain boundaries or dislocations.orioThe insets are fast Fourier transform pattern of the superlattice and is differentofffrom that of the substrate (middle). The inset fast Fourier transform images inoff

Linearly polarized angle (°)

the film thickness (*c* direction) show a much higher carrier mobility in the superlattice than in the polycrystalline or conventionally grown single-crystal sample (Fig. 2a). The grain boundaries in polycrystals markedly reduce carrier mobility<sup>15</sup> (Supplementary Fig. 11). The layered organic spacers make the mobility in conventionally grown single crystals the lowest (Supplementary Fig. 12). Power-dependent the *b*-*c* plane show the structural similarity between the inorganic slab and the substrate (right). Organic atoms are usually invisible under electron diffraction. Scale bars, 6 nm. **c**, Photocurrent measurements with a linearly polarized excitation source showing that the response of the epitaxial layer (top) shows a period that is half of that of a conventionally grown single crystal (bottom). **d**, Transient photovoltage measurements showing the orientation-dependent carrier lifetime in the *a*-*b* plane. The inset optical image shows the measurement setup. The error bars are from measurements of five different devices. Scale bar, 500 μm.

time-resolved photoluminescence measurements show that the superlattice has a longer carrier lifetime than the polycrystal (Fig. 2b), indicating minimal restriction of the carriers. Furthermore, superlattices show better tolerance to high excitation power than polycrystals, suggesting that better crystallinity can reduce material degradation under high excitation power<sup>16</sup>.

50

100

150

200

250

300

350



**Fig. 2** | **Carrier transport properties of the BA<sub>2</sub>SnI<sub>4</sub> superlattice. a**, Transient photocurrent measurements along the film thickness (*c*) direction. The superlattice shows the highest carrier mobility. The carrier mobility in the polycrystal is limited by grain boundaries and lattice misalignments between grains. The conventionally grown single crystal shows the lowest carrier mobility because of the energy barriers caused by the organic spacers along the film thickness direction. The insets show the schematic measurement setups. The error bars are from measurements of five different devices. **b**, Time-resolved photoluminescence measurements showing a longer carrier lifetime in the superlattice than the polycrystal. The lifetime–power relationship in the polycrystal tends to deviate from a linear fit (dashed lines) at high excitation power owing to absorber degradation. The error bars are from measurements of five different devices. **c**, Temperature-dependent *J–V* measurements on solar cells (ITO/ICBA/perovskite/PTAA/Au; active size, 1 mm<sup>2</sup>) fabricated on as-grown films. The current density values are

normalized. As temperature drops, the FF of the superlattice device does not change as strongly as the polycrystal device, indicating a lower internal energy barrier in the superlattice. PTAA, poly[bis(4-phenyl)(2,4,6-trimethylphenyl) amine]. **d**, SEM images and corresponding EBIC mapping of the top surface of BA<sub>2</sub>SnI<sub>4</sub> films. The polycrystal exhibits grain-dependent current signals. The superlattice exhibits stronger current signals with a criss-cross pattern, even with a smooth film surface. Scale bars, 200 nm. **e**, SEM images and corresponding EBIC mapping of the cross section of BA<sub>2</sub>SnI<sub>4</sub> films. The polycrystal exhibits grain-dependent current signals. The superlattice exhibits stronger current signals with a linear pattern. Scale bars, 100 nm. **f**, Thickness-dependent EQE measurements. The superlattice device exhibits a higher EQE with a larger optimal absorber thickness, indicating that the carrier diffusion length in the superlattice is longer than that in the polycrystal. A longer-wavelength collection edge also indicates a smaller bandgap in the superlattice.

The structural advantages of superlattices are validated with temperature-dependent current density–voltage (J–V) characteristics of a BA<sub>2</sub>SnI<sub>4</sub> solar cell. To investigate internal energy barrier for carrier transport, we fabricated a device directly on the superlattice without peeling it off from the epitaxial substrate to minimize any possible confounding factors introduced by the fabrication process<sup>15</sup> (Supplementary Discussion 2 and Supplementary Figs. 13 and 14). As the temperature gradually decreases, thermal energy becomes too small for the carriers to overcome barriers (for example, owing to ionized impurity scattering), so the fill factor (FF) decreases substantially for both superlattice and polycrystalline devices (Fig. 2c). However, the decrease is less pronounced in superlattices, indicating lower internal energy barriers.

We measured the electron-beam-induced current (EBIC) to visualize carrier transport barriers. For polycrystals, the collected currents on the thin film surface heavily depend on grain orientations, indicating disorientated multiple quantum wells (Fig. 2d, left). By contrast, superlattices yield higher and much more uniform currents owing to the well-aligned crystal structure (Fig. 2d, right). Note that superlattices exhibit a criss-cross current pattern owing to their imperfect merging during solution growth (Supplementary Fig. 15). Similar observations can also be made in the sample cross sections (Fig. 2e and Supplementary Discussion 3).

The improved carrier dynamics of superlattices allows a longer carrier diffusion length. As the photovoltaic absorber, the thickness of polycrystals is usually highly restricted<sup>17</sup>, for which the external quantum efficiency (EQE) peaks at about 400 nm for  $BA_2SnI_4$  (Fig. 2f, top). By contrast, the absorber thickness for superlattices can be increased to around 700 nm with enhanced light absorption and, thus, EQE (Fig. 2f, bottom).

We investigated the heteroepitaxial strain in BA<sub>2</sub>SnI<sub>4</sub> superlattices quantitatively by X-ray diffraction. Compared with conventionally grown single crystals, high overall compressive strains are present in superlattices along the *a* and *b* directions, at around 8.59% and around 1.32%, respectively (Fig. 3a, top); a tensile strain of roughly 0.99% is present in the *c* direction owing to the Poisson effect<sup>18</sup> (Fig. 3a, bottom, Supplementary Discussion 4 and Supplementary Table 1). These strains are validated by STEM images (Supplementary Fig. 6 and Supplementary





**Fig. 3** | **Strain properties of BA**<sub>2</sub>**MA**<sub>*n*-1</sub>**Sn**<sub>*n*</sub>**I**<sub>3*n*+1</sub>**superlattices.** *a*, X-ray diffraction measurements of the BA<sub>2</sub>SnI<sub>4</sub> superlattice and conventionally grown BA<sub>2</sub>SnI<sub>4</sub> single crystals. A compressive strain in the *a*-*b* plane and a tensile strain along the *c* direction are observed in the superlattice. **b**, DFT-computed and experimentally calculated lattice strain with different *n* in low-dimensional BA<sub>2</sub>MA<sub>*n*-1</sub>Sn<sub>*n*</sub>I<sub>3*n*+1</sub> perovskites. Crystals with larger *n* will have smaller strain. Inset SEM images show that a larger *n* will result in a smoother surface, which is attributed to fewer defects under smaller epitaxial strain. Scale bars, 50 µm. **c**, Ellipsometry measurements of the dielectric function ( $\varepsilon' + i\varepsilon''$ ) of the BA<sub>2</sub>MA<sub>2</sub>Sn<sub>3</sub>I<sub>10</sub> superlattice and conventionally grown BA<sub>2</sub>MA<sub>2</sub>Sn<sub>3</sub>I<sub>10</sub> single crystals. The larger  $\varepsilon'$  in the superlattice indicates that the



compressive strain can increase the dielectric constant and the Bohr radius in the superlattice. A red shift in  $\varepsilon''$  shows that the compressive strain decreases the bandgap of the superlattice. **d**, Estimated exciton binding energies obtained from temperature-dependent photoluminescence measurements. The smaller fitted exciton binding energy in the superlattice than the polycrystal indicates a weaker quantum confinement effect because of the smaller width of the organic barrier. In the inset equation, *I* is the integrated photoluminescent intensity,  $I_0$  is the integrated intensity at room temperature, *A* is an arbitrary constant,  $E_B$  is the exciton binding energy,  $k_B$  is the Boltzmann constant and *T* is the temperature.

Discussion 4). Structural computation by density functional theory (DFT) further shows a lattice compression of Sn-I slabs from about 6.04 Å to about 5.94 Å in the *a* direction (Supplementary Fig. 16), yielding an approximately 1.66% strain, which is close to the 1.32% strain in the *b* direction; the width of organic spacers is compressed from about 7.00 Å to about 5.98 Å (Supplementary Figs. 16 and 17), corresponding to an approximately 14.6% strain. Therefore, the high compressive strain is mostly accommodated by organic spacers. High strain reduces the stability of superlattices (Supplementary Figs. 18 and 19). For general heteroepitaxial BA<sub>2</sub>MA<sub>*n*-1</sub>Sn<sub>*n*</sub>I<sub>3*n*+1</sub>, as *n* increases, the volume ratio of the Sn-I slabs increases, the overall lattice strain decreases (Fig. 3b) and the structure is more stable. Moreover, lower strain results in fewer structural defects and smoother surfaces (Fig. 3b, inset images).

To avoid structural change and achieve reliable measurements of superlattices, we chose BA<sub>2</sub>MA<sub>2</sub>Sn<sub>3</sub>I<sub>10</sub> (*n* = 3) to study their strain-controlled optoelectronic properties. We used ellipsometry to study the dielectric functions ( $\varepsilon' + i\varepsilon''$ ). The higher  $\varepsilon'$  of superlattices indicates weakened quantum confinement by compressed organic spacers (Fig. 3c), a larger Bohr radius in the multiple quantum wells and, therefore, a higher rate of free-carrier generation<sup>19</sup> (Supplementary Discussion 5). Besides, the shift in  $\varepsilon''$ , which reflects the absorption wavelength<sup>20</sup>, suggests a smaller bandgap in superlattices compared with conventionally grown single crystals, which is also evident by the longer-wavelength collection edge of superlattices (Fig. 2f and Supplementary Fig. 20). Temperature-dependent photoluminescence measurements also show a much-reduced fitted exciton binding energy in superlattices compared with conventionally grown single crystals<sup>18,19</sup> (Fig. 3d). In addition, the carrier lifetime in superlattices is slightly longer than conventionally grown single crystals at 0° in transient photovoltage measurements (Fig. 1d). All these characteristics can be attributed to the weakened quantum confinement in superlattices.

Large heteroepitaxial strains heavily influence the stability of superlattices (Fig. 3b, Supplementary Discussion 4 and Supplementary Figs. 18 and 19). We choose  $BA_2MA_4Sn_5l_{16}$  (n = 5) to investigate the device performance owing to its better stability. To further relieve the strain and create an even more stable structure, we investigated using  $Bi^{3+}$  (103 pm in radius<sup>21</sup>) to partially replace  $Sn^{2+}$  (118 pm in radius<sup>22</sup>). DFT calculations show that the  $Bi^{3+}$  tends to concentrate at the interface between the inorganic slab and the organic spacer to relieve the compressive strain (Fig. 4a, top and Supplementary Fig. 21), forming an aggregated



**Fig. 4** | **Photovoltaic studies of Bi**<sup>3+</sup>-**alloyed superlattice. a**, Structure of the Bi<sup>3+</sup>-alloyed BA<sub>2</sub>MA<sub>2</sub>Sn<sub>3</sub>I<sub>10</sub> superlattice computed by DFT. The Bi<sup>3+</sup> ions preferentially aggregate at the interface between the organic and inorganic slabs to relieve the lattice strain (top). The aggregated Bi<sup>3+</sup> alloying alters the electronic band structure, resulting in a substantially decreased CBM. Combined with the region without Bi<sup>3+</sup>, they form a double-band structure in the inorganic slab (bottom). **b**, Certified photovoltaic performance measurement based on a Bi<sup>3+</sup>-alloyed BA<sub>2</sub>MA<sub>4</sub>Sn<sub>5</sub>I<sub>16</sub> superlattice, showing a bandgap of 1.042 eV and a V<sub>oc</sub> of 0.967 V. **c**, Unusual carrier transport processes with intraband relaxation, resulting in a high V<sub>oc</sub>. Note that both Sn-I and Bi/Sn-I regions are in direct physical contact with the ETL. HTL, hole transport layer.

**d**, Wavelength-dependent *J*–*V* measurements of a polycrystalline solar cell with a uniform Bi<sup>3+</sup> distribution and, therefore, a single bandgap (left) and a superlattice (right) solar cell. In the polycrystalline device, reasonably small variations in the FF indicate that the carrier transport and the collection are almost independent of wavelength; therefore, the abruptly decreased  $V_{oc}$  at about 1,000 nm suggests that the uniform Bi<sup>3+</sup> distribution does not alter the band structure. In the superlattice device, when the incident wavelength is shorter than around 900 nm, neither FF nor  $V_{oc}$  exhibit an obvious wavelength dependency. However, once the excitation wavelength is longer than about 900 nm, both FF and  $V_{oc}$  decrease substantially. **e**, Extracted FF and  $V_{oc}$  form **d**.

Bi<sup>3+</sup> atomic layer to decrease the formation energy (Supplementary Fig. 22 and Supplementary Discussion 6) of the superlattice and yield a more stable structure (Supplementary Fig. 23). Furthermore, the aggregated Bi<sup>3+</sup> alloying decreases the conduction band minimum (CBM) (Fig. 4a, bottom and Supplementary Figs. 24 and 25). The region without Bi<sup>3+</sup> alloying remains intact. The result is an inorganic slab with a double-band structure.

We studied the photovoltaic performance of those superlattices. We chose 10% Bi<sup>3+</sup>-alloyed BA<sub>2</sub>MA<sub>4</sub>Sn<sub>5</sub>I<sub>16</sub> (n = 5) superlattice with a textured surface and fabricated a solar cell directly on the epitaxial substrate (Supplementary Figs. 26 and 27). Indene-C60 bisadduct (ICBA) was used as the electron transport layer (ETL) because its CBM level (Supplementary Fig. 28) is higher than that of the Bi/Sn-I but lower than the Sn-I slabs (Supplementary Table 2). The Bi/Sn-I and the Sn-I regions are both in contact with the ETL. The as-certified superlattice solar cell exhibits a stable 12.36% photoelectric conversion efficiency under the quasi-steady state (Supplementary Fig. 29)-the highest in lead-free low-dimensional perovskite solar cells. To further replace the lead-containing substrate, it is also feasible to use other substrates (Supplementary Figs. 3 and 5) or to exfoliate and transfer the superlattice from the epitaxial substrate to a general substrate (Supplementary Figs. 30, 31 and 32). Moreover, the quantum efficiency of the solar cell (Fig. 4b and Supplementary Fig. 29) shows a carrier collection cut-off at approximately 1,190 nm, which gives a bandgap of about 1.042 eV

and a  $V_{\rm oc}$  of at most 0.802 V according to the Shockley–Queisser limit<sup>23</sup>. However, the certified  $V_{\rm oc}$  is 0.967 V, indicating other contributing mechanisms.

Figure 4c shows the schematic band diagram of the superlattice solar cell. Because the aggregated Bi<sup>3+</sup> alloying in superlattices could lead to a radiative band structure besides the band-tail states that commonly exist in Bi<sup>3+</sup>-doped polycrystals<sup>24-29</sup> (Supplementary Fig. 23 and Supplementary Discussion 6), an intraband relaxation mechanism is possible for contributing to the high  $V_{\rm oc}$ . We performed wavelength-dependent J-V measurements to investigate the potential mechanism (Fig. 4d,e). Under short incident wavelengths (less than about 1,000 nm), most electrons are excited into energy states higher than the CBM of both Sn-I and Bi/Sn-I regions. Those electrons from the Sn-I region naturally relax to the CBM of the Sn-I region. Furthermore, a substantial portion of the electrons from the Bi/Sn-I region can also relax to the CBM of the Sn-I region through intraband relaxation (solid blue arrows in Fig. 4c). This transition is possible because the atomic-thin Bi/Sn-I region is easy for carriers to diffuse across. Also, the built-in potential in the p-i-n structure might have facilitated this atomic-scale transition; moreover, the ETL layer favours electron collection from the Sn-I region (solid red arrow in Fig. 4c). Therefore, most of the carriers are in the Sn-I region, yielding a high V<sub>oc</sub> and a high FF (Fig. 4d,e). Under long incident wavelengths (more than about 1,000 nm), electrons can only be excited in the Bi/Sn-I region. The relatively low-energy

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**Fig. 5** | **Dynamics analysis of hot electrons in Bi**<sup>3+</sup>-**alloyed superlattices. a**, Measured transient absorption spectra for Bi<sup>3+</sup>-alloyed BA<sub>2</sub>MA<sub>2</sub>Sn<sub>3</sub>I<sub>10</sub> superlattice devices. It is clear to see that the device exhibits obvious changes in GSB and ESA intensities with and without the 10-V bias, suggesting bias-dependent hot carrier dynamics in Bi<sup>3+</sup>-alloyed BA<sub>2</sub>MA<sub>2</sub>Sn<sub>3</sub>I<sub>10</sub> superlattice

devices. **b**, Extracted hot carrier relaxation lifetimes from **a** for Bi<sup>3+</sup>-alloyed BA<sub>2</sub>MA<sub>2</sub>Sn<sub>3</sub>I<sub>10</sub> superlattice devices. Their lifetimes show negligible changes with and without the 10-V bias, excluding the influence of the applied bias on the hot carrier lifetimes.

electrons can only relax to the CBM of the Bi/Sn-I region and then to the ETL by means of interband transition (dashed red arrows in Fig. 4c). Therefore, most of the carriers are in the Bi/Sn-I region, contributing to a low  $V_{\rm OC}$  (Fig. 4d,e). The energy barrier between the Bi/Sn-I region and the ETL causes serious charge accumulation (Supplementary Discussion 7), resulting in a low FF (Fig. 4d,e). When the device is excited under mixed incident wavelengths, the high-energy electrons facilitate the quasi-Fermi-level splitting in the Sn-I region. The low-energy electrons will have a relatively small influence on the overall  $V_{\rm OC}$  because of the small portion of long wavelengths (between about 1,000 nm and about 1,200 nm) in the solar spectrum (roughly 9%)<sup>30</sup> and, thus, the small quantity of the low-energy electrons. The overall  $V_{\rm OC}$  is predominantly determined by the bandgap of the Sn-I region (Supplementary Fig. 33 and Supplementary Discussion 7).

To verify this mechanism, we collected pump–probe ultrafast transient absorption spectra to investigate their hot carrier dynamics (Supplementary Discussion 8). To meet the measurement requirement, a transferred device structure (ITO/superlattice/ICBA/polypropylene tape/ITO) (Supplementary Fig. 34) was adopted under an external electrical field to mimic the built-in potential of the solar cell. We measured transient absorption spectra with and without the bias (Fig. 5a and Supplementary Figs. 35 and 36). The polycrystalline thin films exhibit very different spectral profiles from superlattices (Fig. 5a and Supplementary Fig. 35). Obvious ground state bleaching (GSB) signals in the negative intensity region could only be observed in superlattices, indicating more efficient carrier dynamics in the superlattices than those in the polycrystalline thin films.

The lifetime of hot electrons could be obtained by extracting and fitting relaxation time profiles at selected wavelengths (Fig. 5b and Supplementary Fig. 37). The hot electron lifetimes of superlattices (Bi<sup>3+</sup>-alloyed and Bi<sup>3+</sup>-free) are between about 0.35 and 0.36 ps, which are almost twice that of Bi3+-doped polycrystalline thin films (approximately 0.19 ps) (Supplementary Fig. 37). Accordingly, the calculated hot electron diffusion length in superlattices is around 3.9 nm, much longer than the width of the Bi/Sn-I regions (about 0.6 nm) (Supplementary Fig. 37), suggesting that the hot electrons can readily travel across the Bi/Sn-I regions to the Sn-I regions. Furthermore, transient absorption spectra show an obviously enhanced GSB intensity in Bi<sup>3+</sup>-alloyed superlattices when the applied bias increases from 0 V to 10 V (Fig. 5a). By contrast, the excited state absorption (ESA) signal decreases (Fig. 5a). However, no such phenomenon can be observed in Bi3+-free superlattices or Bi3+-doped polycrystalline thin films (Supplementary Fig. 35), supporting the potential intraband relaxation in Bi<sup>3+</sup>-alloyed superlattices: the increased GSB signal intensity indicates

a reduced number of electrons at the ground state in the valence band. Because the excitation setups for 0-V and 10-V measurements are the same, the reduced electrons at the ground state in the valence band are not from a stronger excitation. Therefore, it suggests that the number of electrons relaxing from the conduction band to the valence band after excitation is reduced. However, because the hot carrier lifetime is minimally influenced by the electrical field (Fig. 5b and Supplementary Figs. 37 and 38), those 'reduced' electrons can only transport to Sn-I regions but not to the ITO or ICBA layers because of the direction of the applied electrical field and the strong interfacial barriers, respectively (Supplementary Discussion 8).

The decreased ESA intensities owing to a reduced number of hot electrons in the valence band provide further evidence for the potential intraband relaxation. However, because of the same excitation setup and similar hot electron lifetimes for 0-V and 10-V measurements (Fig. 5b and Supplementary Figs. 37 and 38), the obviously reduced hot electron population is not from a weaker excitation or more rapid relaxation but from other relaxation routes. The excited hot electrons have short lifetimes and can only undergo atomic-scale diffusion to Sn-I regions but not to the ITO or ICBA layers (Supplementary Discussion 8).

Besides the unique intraband relaxation mechanism discussed here, other carrier transport processes might also be possible for the high  $V_{oc}$ , such as the superposition principles between parallel subcells<sup>31</sup>, sub-band absorption<sup>32</sup>, multiple exciton generation in atomic-scale structures<sup>33</sup> and ion diffusions<sup>34</sup>. Further research is required to gain a complete understanding of this phenomenon. Continued improvements in the device performance are possible with optimizations of the design of the electrode patterns, the resistivity of the top electrode and the band alignment of the ETL/hole transport layer.

#### **Online content**

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41586-022-04961-1.

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# Article

# Methods

#### Materials

The materials used in this study were used as purchased without further purification, which included lead iodide (PbI2, 99.99%, Tokyo Chemical Industry), lead bromide (PbBr<sub>2</sub>, 98%, Alfa Aesar), hydrobromic acid (HBr, 48 wt% in water, Sigma-Aldrich), methylamine (CH<sub>3</sub>NH<sub>2</sub>, 40% in methanol, Tokyo Chemical Industry), tin (II) oxide (SnO, 97%, Sigma-Aldrich), hydroiodic acid (57% in water, Sigma-Aldrich), hypophosphorous acid (H<sub>3</sub>PO<sub>2</sub>, 50 wt% in water, Sigma-Aldrich), methylammonium iodide (99.9%, GreatCell Solar), n-butylammonium iodide (99.9%, GreatCell Solar), caesium chloride (CsCl, 99.9%, Sigma-Aldrich), silver chloride (AgCl, 99%, Sigma-Aldrich), antimony (III) chloride (SbCl<sub>3</sub>, 99%, Sigma-Aldrich), bismuth (III) iodide (Bil<sub>3</sub>, 99%, Sigma-Aldrich), ICBA (LT-S9030, Luminescence Technology), poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine](PTAA, LT-N168, Luminescence Technology), chlorobenzene (C<sub>6</sub>H<sub>5</sub>Cl, TCl America), anhydrous dimethylformamide (C<sub>3</sub>H<sub>7</sub>NO, 99.8%, Sigma-Aldrich), anhydrous gamma-butyrolactone (GBL, C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>, 99% Sigma-Aldrich), anhydrous dimethyl sulfoxide (C2H6OS, 99.9%, Sigma-Aldrich), isopropanol (IPA, C<sub>3</sub>H<sub>8</sub>O, 99.5%, Sigma-Aldrich) and methanol (99.8%, CH<sub>3</sub>OH, Sigma-Aldrich).

#### Preparation of single-crystal perovskites

MAPbBr<sub>3</sub>: flat and smooth centimetre-sized bulk MAPbBr<sub>3</sub> single crystals were prepared by solution-based growth<sup>35</sup>. The single crystal was used as the 3D perovskite substrate to grow the low-dimensional perovskite superlattice without any further treatment. MAPbI<sub>3</sub>: MAPbI<sub>3</sub> single crystals were prepared by solution-based growth<sup>15</sup>. The as-obtained crystals were ultrasonically cleaned in an anhydrous IPA solvent for 5 min. Then the crystals were crushed into powders for growth precursor preparation.

#### Synthesis of low-dimensional perovskites

7.5 mmol SnO was added into 10 ml steaming hydroiodic acid (57 wt%) mixed with 2.5 ml  $H_3PO_2$  (50 wt%) aqueous solution until the precursor solution become transparent yellow. Then the stoichiometric n-butylammonium iodide (3 mmol)/methylammonium iodide (6 mmol) methanol solution was injected into the precursor solution under stirring. Later, the beaker was transferred into a vacuum chamber to remove the dissolved oxygen and left standing for crystallization. Crystal flakes would appear after around 2 h. Then IPA was used to wash the crystals three times. Finally, the crystals were dried in vacuum and then directly dissolved in GBL to form the growth solution (0.5 M) for low-dimensional perovskites. For the  $Bi^{3+}$ -alloyed superlattice, 10% molar ratio of Bil<sub>3</sub> was dissolved into the growth solution under room temperature. The solution was filtered before use to remove any undissolved components.

#### Preparation of precursors for mixed and double perovskites

The mixed perovskite MAPb<sub>0.5</sub>Sn<sub>0.5</sub>Br<sub>3</sub> was prepared by mixing MABr, PbBr<sub>2</sub> and SnBr<sub>2</sub> with a 2:1:1 molar ratio in dimethylformamide (1.5 M). The double perovskite Cs<sub>2</sub>AgSbCl<sub>6</sub> precursor solution was prepared by directly mixing CsCl, AgCl and SbCl<sub>3</sub> with a 2:1:1 molar ratio in dimethyl sulfoxide (0.4 M). The as-prepared solution was stirred at 60 °C until the solution became clear. Then adding 0.4 M MAPbl<sub>3</sub> single-crystal powder to the solution completed precursor solution preparation for achieving a suitable lattice constant with minimal lattice mismatch between the substrate and the inorganic slab of the epitaxial layer.

#### **Device fabrication**

 $MAPbBr_{3} bulk crystals were used as the 3D substrates as their synthesis is well established. To further reduce the lattice mismatch, the mixed perovskite (or double perovskite) precursor was hot casted onto the MAPbBr_{3} crystal to form a smooth epitaxial layer, which was the actual$ 

substrate surface for growing the low-dimensional perovskites. The thickness of the smooth epitaxial layer did not influence the subsequent superlattice growth or device fabrication. Polyimide films (12.7 µm thick) were prepatterned (with an opening size of  $1 \mu m \times 1 \mu m$ ) to serve as the growth mask by following a reported method<sup>15</sup>. Then a layer of Au was deposited by sputtering to serve as the bottom electrode. Later, PTAA solution (1.5 mg ml<sup>-1</sup> in anhydrous toluene) was directly spin-coated onto the patterned polyimide/Au films at 2,500 rpm for 30 s, followed by annealing at 80 °C for 3 min. Then the growth substrate was laminated with the polyimide/Au/PTAA mask and then spin-coated by supersaturated mixed perovskite (or double perovskite) precursor at 4,000 rpm for 30 s, followed by annealing at 100 °C for 5 min. Subsequently, low-dimensional perovskite growth solution (0.5 M in GBL) was spin-coated on the substrate at 1.500 rpm for 60 s. followed by annealing at 180 °C for 2 min to form the superlattice absorber layer. After that, ICBA (20 mg ml<sup>-1</sup> in chlorobenzene) was spin-coated onto the epitaxial layer, followed by annealing at 100 °C for 5 min. Finally, a layer of ITO was deposited by sputtering to serve as the transparent top electrode. The polycrystalline devices are fabricated by hot casting<sup>22</sup>.

### DFT calculations

First-principles DFT calculations were performed using the Vienna Ab initio Simulation Package<sup>36</sup>. The projector augmented-wave pseudopotential was used for describing electron-ion interactions<sup>37</sup>. The generalized gradient approximation parameterized by Perdew, Burke and Ernzerhof was used to treat the electron-electron exchange-correlation functional<sup>38</sup>. The van der Waals functional DFT-D3 was applied to properly describe the long-range dispersion interactions between the organic molecules in the hybrid materials<sup>39</sup>. The hybrid functionals within Heyd-Scuseria-Ernzerhof formalism with 70% Hartree-Fock exchange were used to calculate bandgaps for the Sn-based perovskites<sup>40,41</sup>. The wave functions were expanded in a plane-wave basis set with a cut-off energy of 400 eV. The structures for conventionally grown single-crystal Ruddlesden-Popper perovskites and epitaxially grown perovskites were built on the basis of experimental results of the lattices. The atomic positions were fully optimized until all components of the residual forces were smaller than 0.03 eV Å<sup>-1</sup>. The convergence threshold for self-consistent field iteration was set at 10<sup>-5</sup> eV. Γ-centred  $2 \times 1 \times 4$  and  $4 \times 4 \times 1k$ -point grids were used for superlattice and conventionally grown single crystals, respectively. Owing to the limited computational resources, we could only simulate the n = 3 structure. but this would not influence the device (n = 5) because the formation mechanism of the double-bandgap structure was the same.

#### Morphology characterization

All SEM images were taken using a Zeiss Sigma 500 microscope. All optical images were taken using a Zeiss Axio Imager optical microscope.

#### Structure characterization

X-ray diffraction was measured by a Rigaku 393 Smart lab diffractometer equipped with a Cu K $\alpha$ 1 radiation source ( $\lambda$  = 0.15406 nm) and a Ge 394 (220 × 2) monochromator. The STEM images were taken using a cryo-FEI 200 kV Sphera microscope. Samples for the STEM were prepared using a frozen focused ion beam (FEI Scios DualBeam FIB/SEM). The conventionally grown single crystal was hard to be imaged by STEM because the sample without an epitaxial substrate curled quickly owing to its instability in the scanning transmission electron microscope. X-ray photoelectron spectroscopy measurements were carried out using Kratos AXIS Supra with a He I (21.22 eV) source under 10<sup>-8</sup> torr chamber pressure.

#### **Optical characterizations**

Photoluminescence and time-resolved photoluminescence measurements were performed with a confocal microscope system by focusing a monochromatic 6-ps pulsed laser with a 4× objective lens (numerical

aperture 0.13). Optical functions were measured by ellipsometry (J.A. Woollam M-2000D spectroscopic ellipsometer). Ultraviolet photoelectron spectroscopy measurements were carried out using Kratos AXIS Supra with a HeI (21.22 eV) source under 10<sup>-8</sup> torr chamber pressure. Ultraviolet–visible spectroscopy and absorption spectra were collected using a PerkinElmer Lambda 1050 ultraviolet–visible spectroscopy system under the reflection mode.

#### **Electrical characterizations**

Polarized photocurrent was measured with a polarizer. Time of flight was measured by extracting the decay time of the transient photocurrent to calculate the carrier mobility. An external bias of 0.5 V was used to power the devices with a resistor connected in series. Orientation-dependent transient photovoltages were measured with an oscilloscope (Agilent MSO6104A Channel Mixed Signal) to study the carrier lifetime. A pulsed laser with a pulse width of less than  $10^{-10}$  s was used as the light source. The EBIC was collected using a FEI Scios DualBeam microscope with a Mighty EBIC 2.0 controller (Ephemeron Labs) and a Femto DLPCA-200 preamplifier. Lateral Au electrodes were deposited by electron-beam evaporation for surface measurements; a prepatterned Au-coated polyimide film was used as the bottom electrode for cross-section measurements; the top surface was deposited with a layer of Au by electron-beam evaporation to serve as the top electrode. The EBIC and SEM images of the same region of interest were collected simultaneously. The samples were several micrometres in thickness, whereas EBIC could penetrate up to several micrometres into the samples<sup>42</sup>. The transient absorption spectroscopy was performed using an ultrafast transient absorption system with a tunable pump and white-light probe to measure the differential absorption through the sample. The laser system consisted of a regeneratively amplified Ti:sapphire oscillator (Coherent Libra), which delivered 4-mJ pulse energies centred at 800 nm with a 1-kHz repetition rate. The pulse duration of the amplified pulse was approximately 50 fs. The laser output was split by an optical wedge to produce the pump and probe beams and the pump beam wavelength was tuned by an optical parametric amplifier (Coherent OPerA). The pump beam was focused onto the sample by a spherical lens at near-normal incidence (spot size of full width at half maximum (FWHM) about 300 µm). The probe beam was focused onto a sapphire plate to generate a white-light continuum probe, which was collected and refocused onto the sample by a spherical mirror (spot size of FWHM approximately 150 um). The transmitted white light was collected and analysed with a commercial absorption spectrometer (HELIOS, Ultrafast Systems LLC). Pulse-to-pulse fluctuations of the white-light continuum were accounted for by a simultaneous reference measurement of the continuum. The pump wavelength was maintained at 610 nm with a pulse power of 100 nJ (or approximately 80 µJ cm<sup>-2</sup>). The pump and probe beams were linearly cross-polarized and any scattered pump light into the detection path was filtered by a linear polarizer. The time delay was adjusted by delaying the pump pulse with a linear translation stage (minimum step size 16 fs). The individual component kinetic traces were fit to biexponential decays by least squares means.

#### Photovoltaic characterizations

J-V measurements were carried out using a Keithley 2400 source meter under a simulated air mass of 1.5 irradiation (100 mW cm<sup>-2</sup>) and a xenon-lamp-based solar simulator (Oriel LCS-100). Temperaturedependent J-V measurements were performed with the sample in a liquid-nitrogen-cooled metal tank, in which one side was glass to allow illumination. The same configuration was used for both epitaxial and polycrystalline devices. EQE data were collected by illuminating the device under monochromatic light using a tungsten source (chopped at 150 Hz) while collecting the photocurrent by a lock-in amplifier in the alternating current mode. The 2D mapping of the thickness-dependent EQE was generated from the Contour-Color Fill function. Wavelength-dependent *J*–*V* measurements were carried out by applying a series of bandpass filters (FWHM about 150 nm) under the solar simulator to measure both the polycrystalline and epitaxial devices.

#### **Data availability**

All data are available in the manuscript or supplementary materials.

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Author contributions S.X. and Y. Lei conceived the idea. Y. Li carried out the DFT calculations. Y. Lei, C.L. and R.W. synthesized the materials, prepared the substrates and fabricated the devices. Y. Lei, Q.Y., S.Z., H.G. and Y.C. contributed to the structural characterizations. S.Z. contributed to the grazing-incidence wide-angle X-ray scattering characterizations. F.B. and Y.W. contributed to the transient absorption spectroscopy characterizations. J.Z. contributed to the optical and electrical characterizations. R.Z. carried out the Fourier transform infrared spectroscopy characterizations and the simulations. All authors contributed to analysing the data and commenting on the manuscript.

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#### Additional information

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1	Supplementary Information for:
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4	Perovskite superlattices with efficient carrier dynamics
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#### 33 Supplementary Discussion 1: Epitaxial superlattice structure.

Low-dimensional perovskites show improved long-term stability due to the hydrophobic 34 35 organic surface terminating ligands<sup>1</sup> and hysteresis-free electrical transport, probably because of the high exciton binding energy of the multiple-quantum-well<sup>2</sup>. Unlike the traditional three-36 37 dimensional (3D) metal halide perovskite (e.g., MAPbBr<sub>3</sub> and MAPbI<sub>3</sub>; MA=methylammonium), low-dimensional perovskites are composed of two parts: the 38 39 inorganic slab and the organic spacer<sup>3</sup>. In the inorganic slab, the structure (metal-halide frameworks and the organic cations) is the same as that of the traditional 3D perovskite. 40 41 However, because of the existence of the organic spacer (e.g., BA and PEA; BA=butylamine; 42 PEA=phenethylammonium), the continuous crystal structure in the 3D perovskite is split 43 evenly into periodic two-dimensional (2D) layered structures, which results in a natural 44 multiple-quantum-well. Therefore, the major difference between the 3D and low-dimensional 45 perovskites is the layered organic spacers, which determine the *n* value (i.e., the layer of the inorganic slabs) of the chemical formula  $B_2A_{n-1}M_nX_{3n+1}$  (e.g.,  $B = R-NH_3^+$ ;  $A = CH_3NH_3^+$ , 46  $HC(NH_2)_2^+$ ,  $Cs^+$ ,  $Rb^+$ ;  $M = Pb^{2+}$ ,  $Sn^{2+}$ ;  $X = Cl^-$ ,  $Br^-$ ,  $I^-$ ) for low-dimensional perovskites. 47

In polycrystals, low-dimensional perovskites cannot form a long-range order due to the misaligned orientations of the inorganic slabs<sup>2, 4, 5</sup>, representing the major limiting factor for achieving highly efficient carrier dynamics<sup>5-9</sup>. Bulk single crystals are valuable for studying fundamental material properties of low-dimensional perovskites but are less useful for building devices that usually require thin films. Thin plates of single-crystal low-dimensional perovskites have been demonstrated<sup>10-12</sup>, but due to their natural growth behavior, those thin plates are usually made of large-area inorganic slabs stacking on top of another, so they have only in-plane carrier transport within the slab but not out-of-plane carrier transport between the slabs as required for building high-performance electronic devices<sup>10, 11</sup>. Specifically, carriers can transport along the inorganic slabs very efficiently, but when they travel across to the insulative organic spacers, strong recombination and trapping will take place. Even though 3D/2D thin films have been studied, the 2D components were only introduced to passivate 3D perovskites<sup>15-19</sup> but not to engineer the 2D structure. As a result, the orientation, lattice strain, and carrier dynamics of formed low-dimensional perovskites are still uncontrollable.

The low-dimensional perovskite superlattice reported in this work overcame these challenges. BA<sub>2</sub>SnI<sub>4</sub> (*n*=1) is the most challenging for engineering the quantum mechanics to achieve high-efficiency carrier dynamics compared to higher n-value quasi-2D perovskites, which usually forms the horizontally aligned quantum-well structure and has the highest exciton binding energy and, therefore, the worst carrier dynamics. Therefore, we chose BA<sub>2</sub>SnI<sub>4</sub> as an example to study its growth mechanism and intrinsic electrical properties.

68 The superlattice could be obtained by a heteroepitaxial growth method (Supplementary 69 Fig. 2). In this epitaxial system, because the substrates were still perovskites, they were able to 70 form strong metal-halide ionic bonds with the inorganic slabs (Fig. 1b)<sup>13-15</sup>, which was much 71 stronger than the weak Van der Waals forces between the substrate and the organic spacers in 72 the low-dimensional perovskite layer. In this case, we could use chemical bonds to selectively 73 anchor different facets in the low-dimensional perovskites to realize accurate quantum-well 74 alignment, as well as orientation control. In addition, the growth along horizontal orientations 75 (Supplementary Fig. 1a and 1b) was not considered to be stable because it was not energetically favorable to form horizontal epitaxial layers where a complete organic or inorganic layer was 76

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grown on the substrate as the first layer, which would otherwise contain a perovskite layer of an infinite n, a thermodynamically unstable structure<sup>16</sup> (Supplementary Fig. 1).

Therefore, the epitaxial layer formed a vertically aligned rather than a horizontally aligned structure (Fig. 1a and 1b; Supplementary Figs. 1, 2, and 3). The vertically aligned structure could be visualized by both scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM), showing apparent morphology differences from traditional 2D and 3D perovskites.

84 Besides the epitaxial orientation, the as-grown crystals were also found to exhibit a plate 85 with crisscross morphologies (Fig. 1a; Supplementary Figs. 2 and 3). The reason originated from the growth rate and substrate. In general, the growth rates of perovskites along the 86 87 horizontal or vertical directions can be controlled by tuning the growth temperature and the 88 precursor concentration. At a low growth temperature, the growth rate in all directions is low 89 because of the temperature-reversal growth behavior. Then the growth rate is surface reaction 90 controlled. The precursor molecules have sufficient time to diffuse and adsorb at the most 91 energetically favorable locations. The tri-phasic interface between the 3D perovskite substrate, 92 the epitaxial low-dimensional perovskite, and the growth solution is more favorable for 93 nucleation and growth than the bi-phasic interface between the epitaxial low-dimensional 94 perovskite and the growth solution. Therefore, the precursor molecules would prefer to adsorb 95 at the tri-phasic boundary, which contributes to the growth in the horizontal directions (i.e., 96 along the substrate surface). This is also probably why in the literature, almost all of the freestanding bulk single crystals have footprints on the substrate larger than thicknesses<sup>17-19</sup>. 97 The same analysis applies to the scenario when the growth rate is low at a low precursor 98

99 concentration. On the other hand, a high growth temperature and a high precursor concentration 100 lead to growth along the vertical direction (perpendicular to the substrate). Because of the high 101 growth rate under the high temperature and high concentration, the crystal would quickly 102 consume the precursor molecules in their vicinity. The growth rate is diffusion controlled. 103 Precursor molecules would be depleted in regions among the crystals, and therefore the growth 104 along the horizontal directions is slowed down or limited due to the internal competition for 105 precursor molecules. Then the growth rate would be dependent on the precursor diffusion from 106 the bulk solution, which is from the vertical direction of the crystals. Fresh precursor molecules 107 would first arrive at the top surface of the crystals and thus contribute to the fast growth along 108 the vertical direction of the crystals. In this epitaxial process, the substrates in this study (e.g., MAPb<sub>0.5</sub>Sn<sub>0.5</sub>Br<sub>3</sub>) all had a cubic lattice structure<sup>20</sup>, suggesting that the lattice parameters in the 109 110 a and b directions are symmetric. There would not be any differences if the epitaxial crystal 111 plates were growing along the *a* or *b* direction. As a result, the chances for the epitaxial crystal 112 plates to grow along the a and b directions were theorectically 50%-50%. Therefore, the as-113 grown epitaxial layers exhibit two perpendicular crisscross morphologies.

Besides, it was also worth pointing out that even though we also used spin coating as an approach, it was only a way to generate a uniform coating of the growth solution. The growth still followed an epitaxial growth mechanism, a much slower kinetic process, which was entirely different from that of the traditional spin coating method. In the traditional spin coating method for making low-dimensional perovskite thin films, the preparation of their precursor solution was usually done by a simple mixture of organic and inorganic materials under calculated molar ratios. Also, volatile solvents or co-solvents (e.g., dimethyl sulfoxide (DMSO); dimethylformamide (DMF); DMF/DMSO) were typically used<sup>2, 21</sup>. Some other approaches,
such as antisolvents<sup>22</sup> and hot-casting<sup>2</sup>, were used to accelerate crystallization and obtain highcoverage and uniform films. Low-dimensional perovskite films could usually be formed during
the spin coating process, which was also an indicator for its highly dynamic process. In this
way, it was challenging to obtain component-pure high-*n* value 2D perovskites.

126 In the spin coating process of this work, there were three key fundamental differences:

127 1. Traditional spin coating was done on non-perovskite substrates (e.g., ITO (indium tin
 128 oxide) or FTO (fluorine-doped tin oxide), electron transport layer (ETL), or hole transport layer
 129 (HTL)). The spin coating in this work was performed on a single-crystal perovskite substrate.
 130 Only when the spin coating was on a single-crystal perovskite substrate, it was possible to
 131 trigger the chemical epitaxial growth of low-dimensional perovskite superlattice.

132 2. In this work, we used non-volatile  $\gamma$ -Butyrolactone (GBL) as the solvent to prepare the 133 precursor solution. After spin coating, the surface was still wet with a clear precursor solution, 134 and up to this point, no crystallization happened. Only the subsequent high-temperature 135 annealing (e.g., >120°C) could slowly evaporate the solvent and start the epitaxial growth. 136 However, in the traditional spin coating process, the crystallization of low-dimensional 137 perovskites was almost instant.

3. The precursor solutions we used were not a simple mixture of organic and inorganic materials under calculated molar ratios. In contrast, they were prepared by dissolving lowdimensional perovskite single-crystal flakes with certain n values, which had been reported for making high-n value low-dimensional perovskites<sup>2, 16</sup>. Those single-crystal flakes had been synthesized and purified, and flakes with different n-values had slightly different synthesis methods<sup>3, 23</sup>. Therefore, by using the flake-redissolved precursor solutions, the *n*-values in the
as-grown superlattice materials were considered to be highly pure.

145 The verification of the purity of *n* values is shown in Supplementary Fig. 4. It is clear to 146 see that different single-crystal flakes (Supplementary Fig. 4a) exhibited different but distinct 147 photoluminescence (PL) signals (Supplementary Fig. 4b), suggesting that they were not component-mixed crystals<sup>24</sup>. Besides, we had also prepared corresponding precursors and 148 149 fabricated polycrystalline thin films by spin coating. Similarly, both UV-vis (Supplementary Fig. 4c) and PL (Supplementary Fig. 4d) results of those samples exhibited distinct signals that 150 151 were not likely to be composed of a multiple-*n*-value structure, indicating that the superlattice 152 was not composed of a mixed *n*-value structure.

153

### 154 Supplementary Discussion 2: *In-situ* devices.

155 The fabrication of *in-situ* superlattice devices is illustrated in Supplementary Fig. 13. In short, the epitaxial growth of superlattices was based on a single crystal 3D perovskite (e.g., 156 157 MAPb<sub>0.5</sub>Sn<sub>0.5</sub>Br<sub>3</sub>). In this work, the patterned opening has a size of 1  $\mu$ m by 1  $\mu$ m with a pitch 158 of 0.5 cm by 0.5 cm. Then we sputtered a ~100 nm thick layer of Au, followed by spin coating 159 a ~100 nm layer of poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), on top of the 160 patterned polyimide thin film. The Au and PTAA served as the bottom electrode and HTL in the solar cell, respectively. Because the polyimide was already patterned, the as-deposited 161 162 Au/PTAA layers were also naturally patterned (Supplementary Fig. 14a). The patterned 163 polyimide/Au/PTAA layers were very thin and mechanically flexible, so we could tightly and conformally laminate them on top of a smooth 3D perovskite substrate as the growth mask. We 164

165 used PDMS or scotch tape to seal the mask on the mask edges. After that, a thin layer of precursor solution was spin-coated on top of the mask at a rate of 4000 rpm/s to allow the 166 167 solution to fill all patterned openings. The precursor solution had the same composition as that for growing the 3D perovskite substrate, which led to the epitaxial growth of a thin layer of 168 169 substrate on top of the mask during annealing. Finally, another layer of precursor solution for 170 growing the low-dimensional perovskites was spin-coated at a spin rate of 1500 rpm, followed 171 by annealing to trigger the growth of epitaxial superlattices. Different annealing times led to 172 different morphologies of the superlattice (Supplementary Fig. 2).

173 In this process, the very thick single-crystal substrate only served as the substrate to attach the patterned mask layers and support the growth of the epitaxial substrate layer. The thin 174 175 epitaxial substrate layer was used as the template to support the epitaxial growth of low-176 dimensional perovskite superlattices, which ensured full contact between the substrate and the 177 superlattice to minimize interfacial growth defects such as lattice dislocations. For example, if 178 there were no epitaxial substrate layer (Supplementary Fig. 14b), the superlattice in the dashed 179 boxes would only contact PTAA. In this case, epitaxial growth could not be initiated by the 180 PTAA, but only by a "horizontal merging process" from the existing epitaxial superlattices 181 located on top of the patterned openings. Because the horizontal merging was not perfect, the 182 defect density might be high (Supplementary Fig. 15). Therefore, the epitaxial substrate layer was necessary and also integrated into the solar cell between the PTAA (HTL) and superlattice 183 184 (absorber) layers.

185 The as-fabricated *in-situ* devices based on this method were not likely to be practical for 186 high-performance device applications though. Both holes and electrons in perovskites had

limited diffusion lengths. Interfacial charge recombination was critical for the perovskite 187 devices performance. This epitaxial substrate layer not only increased the overall thickness of 188 189 perovskite layers, but also introduced an additional interface for holes to overcome, which 190 increased charge recombination. Therefore, the thickness of the epitaxial substrate layer would 191 influence the extraction of holes in solar cells and the eventual device performance. With the 192 current fabrication parameters, 4000-rpm spin coating of a supersaturated GBL solution 193 produced a 200 nm ~ 300 nm epitaxial substrate layer. We kept the same procedural parameters for all different batches of devices. 194

195 Besides, they were based on a patterned bottom Au/HTL layers and a continuous electron 196 transport layer/top ITO electrode. Because of the unbalanced size of the bottom and top 197 electrodes (Supplementary Fig. 14b), only parts of the superlattice layer would be activated 198 under illumination of the superlattice absorber (the dashed square in Supplementary Fig. 14b 199 top). In this way, a large part of the superlattice layer was wasted. Additionally, the top electrode was homemade ITO, whose sheet resistance was not comparable to that of 200 201 commercial ITO glasses, strongly limiting the solar cell performance. Therefore, the device 202 performance could potentially be largely improved if we balanced the sizes of the top and bottom electrodes and adopt a transfer process to fabricate devices<sup>15</sup>. Moreover, *in-situ* 203 204 superlattices and their devices could not exhibit a promising stability due to the large 205 heteroepitaxial strain, making those *in-situ* devices less practical.

However, because this work focuses on the new superlattice structure and its efficient carrier dynamics, the devices in this work were *in-situ* fabricated so that we could exclude those confounding influences from fabrication steps<sup>15</sup>. The certified superlattice solar cell was integrated with a bulk  $MAPb_{0.5}Sn_{0.5}Br_3$  substrate. In that case, the substrate only served as the template to support the growth of the superlattice and was not a functional component in the fabricated solar cell.

An epitaxial lift-off and transfer step works better for the device performance, but that would prevent us from studying the fundaments of superlattices (e.g., exciton binding energy, strain-induced ion aggregation, and atomic-scale band structure). Thus, we did not introduce the epitaxial lift-off and transfer in this work but only focused on the strained *in-situ* device. The solar cell certificate in this work mainly served to: confirm the efficient carrier dynamics in the low-dimensional perovskite superlattice and prove the unusually high open circuit voltage ( $V_{OC}$ ).

219

### 220 Supplementary Discussion 3: EBIC mapping.

221 We used EBIC mapping to visualize the surface current of different low-dimensional 222 perovskites. The factors that would influence the current include the bandgap and the carrier 223 recombination centers. In Fig. 2d and 2e, the current mapping results from the polycrystalline 224 samples showed a non-homogenous feature, indicating that different grains exhibited different 225 carrier collection efficiencies, which was attributed to the random crystal orientations in those 226 grains. Besides, the lowest current signals always appeared at the grain boundaries, suggesting 227 that the polycrystalline structure suffered from serious carrier recombination, particularly at 228 the grain boundaries.

In contrast, the epitaxial superlattice samples showed very different signals. Even though the SEM images exhibited flat surface morphologies, the EBIC signals captured

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231 simultaneously showed crisscross or linear signal features. Such a phenomenon was from the imperfect crystal merging during the processes of forming the epitaxial thin film, which was 232 233 almost impossible to avoid due to the thin plate merging. Also, because of the strong lattice strain, the possibility for crystallography defects (e.g., lattice misorientation and dislocations 234 235 between the organic spacers and the inorganic slabs) was relatively high (Fig. 3b; 236 Supplementary Fig. 15). SEM imaging is based on scattered electrons at the sample surface, 237 while EBIC can collect current signals several micrometers deep into the samples. Therefore, those defects, even though not visible at the surface by SEM, were captured in EBIC. 238 239 Additionally, the signal intensity was much higher in the superlattice samples than that in the polycrystals due to the enhanced carrier generation and collection, which were attributed to the 240 241 reduced energy bandgap (Supplementary Fig. 20) and transport barriers, respectively.

242

#### 243 Supplementary Discussion 4: Lattice strain.

244 The strain was caused by the lattice mismatch between the substrate and the epitaxial layer<sup>13</sup>. In traditional 3D perovskites, the lattice strain was usually very small. Otherwise, the 245 epitaxial layer would not grow at the first place because the large strain energy would 246 247 significantly increase the barrier for nucleation. However, in low-dimensional perovskites, a 248 large composition is the relatively soft organic spacers. Therefore, the structure becomes more deformable and can tolerate larger strain levels<sup>25-28</sup>. As a result, even though the strain between 249 250 the inorganic slabs and the substrate was still small, the strain between the organic spacers and 251 the substrate could be much larger.

252 In the low-dimensional perovskite superlattice, each inorganic slab was epitaxially grown on the substrate through metal-halide ionic bonds. In this way, the organic spacers (BA, ~0.700 253 nm in conventionally grown single crystals<sup>29</sup>) in between the inorganic slabs would be 254 255 compressed by the adjacent inorganic slabs to fit into a single lattice unit (~0.596 nm) of the 256 substrate (Fig. 1b). The organic spacers would not be stretched over two lattice units (~1.192 257 nm) of the substrate, which would otherwise cause too large strain to be thermodynamically 258 stable. Therefore, the overall lattice strain was from two aspects: the inorganic slab, which was 259 relatively small, and the organic spacer, which was relatively large.

260 In Fig. 3a, the x-ray diffraction (XRD) results were used to calculate the overall lattice constants along the a, b, and c directions of the low-dimensional perovskites. The material in 261 262 those measurements corresponds to n = 1. The Sn-I bonds (in conventionally grown single 263 crystals) in the *a-b* plane were treated the same as those in their 3D counterparts<sup>30, 31</sup>. Therefore, 264 the first peak at 14.66° in the *a-c/b-c* plane of the conventionally grown single crystal was used to calculate the *d*-spacing between two Sn atoms. According to Bragg's Law, the calculated *d*-265 266 spacing was ~6.04 nm in both b and c directions. And the first peak at 6.77° in the a-b plane of 267 the conventionally grown single crystal was also used to calculate the *d*-spacing between two 268 Sn atoms along the *a* direction, resulting in a *d*-spacing of  $\sim$ 13.04 nm.

Similarly, the first peak at 14.50° in the *a*-*c/b*-*c* plane of the superlattice was used to calculate the *d*-spacing in the *c* direction, which was ~6.10 nm. Therefore, the tensile strain along the *c* direction was (6.10-6.04)/6.04 = 0.99%. Additionally, the first peak at 7.41° in the *a-b* plane of the superlattice was used to calculate the *d*-spacing in the *a* direction, ~11.92 nm. Therefore, the compressive strain along the *a* direction was  $(11.92-13.04)/13.04 \approx -8.59\%$ . Finally, together with the STEM analysis, the compressive strain along the *b* direction was (6.04-11.92/2)/6.04 = 1.32%.

In the calculations, we only used the first peak because the other peaks were the multiple-order diffractions of the first peak.

278

#### 279 Supplementary Discussion 5: The dielectric confinement.

280 The low-dimensional perovskites contain alternating inorganic slabs and organic spacers. 281 The dielectric constants of those two parts are very different, where the dielectric constant of 282 the inorganic slabs is much larger than that of the organic spacers, resulting in strong dielectric confinement<sup>32</sup>. Therefore, due to the large compressive strain, the dielectric constant in organic 283 284 spacers was increased, indicating that the difference between the inorganic slabs and the 285 organic spacers was smaller, which resulted in weakened dielectric confinement. Additionally, the compressed thickness of organic spacers led to reduced barrier width of the multiple 286 287 quantum well and therefore weakened dielectric confinement.

288

# 289 Supplementary Discussion 6: Bi<sup>3+</sup> alloying.

The epitaxial growth of low-dimensional perovskites on traditional 3D perovskites introduced enormous lattice strains. Even though the BA could tolerate the structural deformation to a certain extent, the compression from the organic spacers to their adjacent inorganic slabs could still cause structural failure of the Sn-I slabs from their original black phase to a transparent phase in just several days (Supplementary Fig. 19). The degradation rate was found to be highly related to the *n*-value in the general formula of low-dimensionalperovskites (Supplementary Fig. 18). The smaller the *n*, the more rapid the degradation.

297 For example, when n = 1, the width of a unit cell in a conventionally grown single crystal 298 (containing one inorganic slab and one BA) is 0.604 nm + 0.7 nm = 1.304 nm, which would be 299 fitted into two unit cells of the 3D perovskite substrate whose width is 0.596 nm + 0.596 nm =300 1.192 nm, resulting in an overall epitaxial strain of 8.59% (Supplementary Table 1). As the n 301 value increases, the volume ratio of the inorganic slabs gets larger. Even though the lattice strain between the inorganic slabs and the substrate does not change, the overall epitaxial strain 302 303 is reduced (Fig. 3b). For n = 5, the overall strain is calculated to be 3.87%. Additionally, a high 304 *n*-value inorganic slab can tolerate stronger compressive forces applied by the organic spacers 305 because there are multiple inorganic layers to help share the force.

Even though high *n*-value epitaxial layers were more stable, they still underwent phasechange from black to transparent in usually less than 3-5 days (Supplementary Figs. 18, 19, and 23), which was challenging for device fabrication as well as practical applications. Therefore, it was necessary to find a strategy to reduce the strain and improve their stability further.

Reducing the lattice constant of the epitaxial layer by alloying/doping small sized-ions can potentially reduce the strain in the superlattice and thus enhance its stability.  $Bi^{3+}$  was chosen as a smaller metal ion to partially replace the  $Sn^{2+}$  to release more space for the BA. Density Functional Theory calculations were carried out to evaluate the effect of  $Bi^{3+}$  alloying. Perovskite with n = 3 was adopted as a model in this work because it contained both MA and BA, and its structural complexity can be afforded by the computational capacity in this work (Supplementary Fig. 21). Calculation results showed that the Bi<sup>3+</sup> was more likely to replace the Sn<sup>2+</sup> close to the BA to achieve a lower total energy of the entire lattice. When the replacement site was further away from the BA, the total energy became larger. Therefore, Bi<sup>3+</sup> preferably aggregated at the BA/inorganic slab interface (Supplementary Fig. 22).

The calculations also revealed that the aggregated Bi<sup>3+</sup> alloying could vastly change the band structure (Supplementary Figs. 24 and 25): a much-decreased conduction band minimum (CBM) with an almost unchanged the valence band maximum (VBM) at the Bi<sup>3+</sup> aggregated interfacial region. Therefore, the Bi<sup>3+</sup> alloying resulted in a double-band structure in the inorganic slabs, where the alloyed Bi/Sn-I region showed a smaller bandgap than the intact Sn-I region, due to the strain-induced Bi<sup>3+</sup> ion aggregation.

327 However, the PL characterization showed two kinds of phenomena, where both radiative 328 emission and non-radiative emission were found at different excitation areas on the same 329 sample (Supplementary Fig. 23b). The non-radiative emission suggested that sub-band tail states were formed, which was attributed to the Bi3+ doping. The strong radiative emission 330 suggested an altered electrical band structure, which was attributed to the aggregated Bi<sup>3+</sup> 331 alloying. Because Bi3+ ions were impossible to be perfectly aggregated at the interface 332 throughout the entire sample area, the co-existence of doping/alloying resulted into two kinds 333 334 of PL results.

335

#### 336 Supplementary Discussion 7: Intra-band exciton relaxation.

337 In principle, the  $V_{OC}$  of a photovoltaic device was determined by the internal quasi-fermi-338 level splitting, which always stayed inside the bandgap of the absorber. Photovoltaic devices based on the  $Bi^{3+}$  alloyed low-dimensional perovskite superlattice were found to exhibit a largely improved  $V_{OC}$  (Supplementary Fig. 29). The carrier collection cutoff of the solar cell is determined by the component of the lowest bandgap, i.e., 1.042 eV of the Bi/Sn-I region in this case. This low bandgap region did not affect the overall  $V_{OC}$  of the final device. The observed high  $V_{OC}$  suggests unusual electron transport mechanisms in the superlattice.

To investigate the mechanism, we performed wavelength-dependent current densityvoltage (*J-V*) measurements on both superlattice and polycrystalline devices (Fig. 4d). The polycrystalline devices also contained the same concentration of, but uniformly mixed,  $Bi^{3+}$ .

347 We extracted the corresponding  $V_{OC}$  and fill factor (F.F.) to evaluate carrier collection efficiencies (Fig. 4e). It showed that the F.F. in the polycrystalline devices was maintained to 348 349 be ~0.3-0.4, which was relatively constant at different wavelengths of the incident light, 350 because the band tail states (e.g., traps that are introduced by Bi<sup>3+</sup> doping) of the thin film was 351 uniform. In contrast, the F.F. in the superlattice devices kept  $\sim 0.7$  when the incident light wavelength was less than ~900 nm and began to drop to ~0.15 when the incident light 352 353 wavelength was ~1100 nm. The  $V_{OC}$  of the polycrystalline devices fluctuated within a 354 reasonable range due to their defective band tail states and abruptly dropped at ~1000 nm due 355 to the below-band weak absorption (e.g., when the incident light wavelength was  $> \sim 1000$  nm, 356 the device was no longer working). However, even though the Voc of the superlattice devices also began to drop when the incident light wavelength was at ~900 nm, the device still exhibited 357 358 a working condition with a  $V_{OC}$  of ~0.45 V when the incident light wavelength was ~1100 nm. 359 Those results clearly revealed that the excitation energy was critical for the superlattice devices, and the band structure of superlattice devices was different from that of polycrystalline devices. 360

Structural computation illustrated that Bi<sup>3+</sup> ions in the superlattice concentrated at the 361 interface between the inorganic slab and the organic spacer to form an atomic-level alloyed 362 363 layer. As a result, the superlattice exhibited an additional atomic-level heterostructure, which 364 led to a different atomic-level electronic band structure (Bi/Sn-I region, Supplementary Fig. 365 23b). Due to the vertically aligned superlattice structure, the Bi/Sn-I region and the Sn-I region 366 in the inorganic slabs were connected to the ETL simultaneously (Fig. 4c). Under excitation, 367 the electrons at the high-energy states could come from both the Bi/Sn-I and the Sn-I regions. During the high-energy electron relaxation process, those electrons generated from the Sn-I 368 369 region will relax to the Sn-I region to be extracted by the ETL layer. Moreover, those highenergy electrons (higher than the CBM of the Sn-I) generated from the Bi/Sn-I region could 370 371 also relax, by intra-band diffusion, to the Sn-I region rather than to the Bi/Sn-I region.

In this way, if the excitation energy was higher than the bandgap of the Sn-I region, the *V*<sub>OC</sub> magnitude was mainly determined by the energy level of the ETL and the band tail states near the VBM of the Bi/Sn-I region, which is not related to the bandgap of the Bi/Sn-I region. When the excitation energy was less than the bandgap of the Sn-I region but higher than the bandgap of the Bi/Sn-I region, the  $V_{OC}$  magnitude was mainly determined by the energy level of the band tail states near the CBM and the band tail states near the VBM in the Bi/Sn-I region, which resulted in a low  $V_{OC}$ .

Under mixed excitation energies, those high-energy electrons, which were excited by the short-wavelength from both Bi/Sn-I and Sn-I regions to states higher than the CBM of the Sn-I region, were extracted by the ETL, indicating that the quasi-fermi-level splitting was mainly determined by the Sn-I region, which results into a high  $V_{OC}$ . In the meantime, those lowenergy electrons excited by the long-wavelength only exist in the Bi/Sn-I and cannot efficiently
transport to the CBM of the Sn-I or the ETL—they could not be either directly extracted by the
ETL or transport to the Sn-I region. Their energy and quantity are both low, which minimally
impacts the overall *Voc* of the device.

387 In contrast, if a Bi/Sn-I based and a Sn-I based photovoltaic devices were fabricated 388 separately and directly connected in parallel by external cables, the overall output voltage of 389 this combined module would be equal to the output voltage of the Bi/Sn-I one because this 390 integrated module would be two standard power sources connected in parallel. In addition, 391 even when two separate photovoltaic devices were in close contact with each other (e.g., as 392 defined by advanced lithography), their absorber material dimensions could not support the 393 inter-band hot carrier transport because the rapid relaxation of these hot carriers would prevent 394 from transporting between the two absorbers of the separate devices<sup>33, 34</sup>.

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396 Supplementary Discussion 8: Pump-probe ultrafast transient absorption spectrum
 397 measurements.

In the PL spectra (red curves in Supplementary Fig. 23b), the majority of free electrons relax to the low CBM of Bi/Sn-I regions, but there is still a small peak at the lower wavelength from the Sn-I region. However, the observed high *Voc* indicates that the quasi-fermi-level splitting is not determined by the Bi/Sn-I bandgap, which seems to be contradictory to the PL results.

403 To explain this phenomenon, we developed an "intra-band relaxation" mechanism in the 404 above discussions. Many hot electrons generated in the Bi/Sn-I region could relax to the CBM 405 of the Sn-I region; then, these hot electrons could be extracted by the ETL together with the
406 electrons excited in the Sn-I region, resulting in the unusually high *Voc*.

407 The reason why we think this intra-band relaxation mechanism is possible is three-fold:

The atomic-scale thickness of Bi/Sn-I regions means ultra-short carrier diffusion
 length and thus an ultra-short diffusion time.

2. The solar cell structure here is a p-i-n junction. Under the solar cell structure, the builtin potential might facilitate the atomic-scale relaxation of hot electrons from Bi/Sn-I regions to
Sn-I regions, which is different from the situations with only perovskite material (e.g., during
the PL measurement).

3. The CBM position of the ETL favors carrier extraction from only the Sn-I regions, as
evidenced by the UPS and UV-vis data in the Supplementary Table 2.

To gain more understanding on the possibility of this intra-band relaxation mechanism, we have measured pump-probe ultrafast transient absorption spectra on the superlattice devices. The working principle of this measurement is shown in Supplementary Fig. 36. To verify the atomic-scale hot electron diffusion, we studied their relaxation time to calculate the diffusion length. Additionally, to verify the hot electron relaxation from Bi/Sn-I regions to Sn-I regions facilitated by the built-in potential in the solar cell, we measured the transient absorption spectrum under biased and unbiased conditions.

Because the *in-situ* fabricated solar cell contains a bulky non-transparent substrate and the transferred solar cell includes a non-transparent Au electrode, we could not measure anyone of them in the pump-probe equipment. Alternatively, we used a different device structure where an external electrical field could be applied to mimic the built-in potential of the solar cell. The

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427 detailed fabrication processes and device structures for both superlattice and polycrystalline thin-film devices are shown in Supplementary Fig. 34. In this structure, two ITO glass slides 428 429 serve as transparent electrodes. A transparent double-sided tape made of polypropylene (~25 430 um in thickness; 7 eV in bandgap; without any delocalized electrons for holding or transporting electrons<sup>35</sup>) serves as an insulation layer to avoid current injection into the superlattices or 431 432 polycrystalline thin films, which mimics the open-circuit working condition. A layer of ICBA 433 was spin-coated on the absorber to serves as the ETL. Superlattices with n=3 were adopted 434 because superlattices with n=5 were challenging to peel off entirely from the epitaxial substrate 435 to fabricate a sample of the required size for ultrafast transient absorption spectrum 436 measurements.

The measured transient absorption spectra for three different samples with and without the bias are shown in Fig. 5 and Supplementary Fig. 35. The polycrystalline thin films (Supplementary Fig. 35a) exhibit very different spectral profiles from superlattices (Fig. 5a and Supplementary Fig. 35b). Obvious ground state bleaching (GSB) (the depletion of the ground state electrons to excited states) signals in the negative intensity region could be observed in superlattices, indicating more efficient carrier dynamics in the superlattices than those in the polycrystalline thin film.

To verify the atomic-scale hot electron diffusions, we extracted their relaxation time profiles at selected wavelengths (Supplementary Fig. 37). By fitting the relaxation profiles using the multiexponential decay, we could derive hot electron lifetimes of those three different samples. The hot electron lifetimes of superlattices ( $Bi^{3+}$ -alloyed and  $Bi^{3+}$ -free) were 0.35 ps~0.36 ps, almost twice that of polycrystalline thin films (~0.19 ps). We chose three different wavelengths (e.g., 967 nm, 1061 nm, and 1303 nm) for each sample to ensure the measured
lifetimes were reasonable, if the derived lifetimes at different wavelengths were similar.

451 Accordingly, the diffusion length for hot electrons can be calculated as:

452 
$$L_D = \sqrt{\frac{K_B \cdot T \cdot \mu \cdot \tau}{e}}$$

where  $K_B$  is the Boltzmann's constant, *T* is the temperature,  $\mu$  is the electron mobility (Fig. 2a),  $\tau$  is the hot electron relaxation lifetime, and *e* is the electron charge. The calculated hot electron diffusion length in polycrystalline thin films (~1.41 nm) was less than half of those in superlattices (Supplementary Fig. 37d). In superlattices, the hot electron diffusion length of the Bi<sup>3+</sup>-alloyed superlattice (~3.86 nm) is more than six times of the width of the Bi/Sn-I regions (~0.6 nm), suggesting that the hot electron can readily travel across the Bi/Sn-I regions to the Sn-I regions.

460 To verify the hot electrons relaxation from Bi/Sn-I regions to Sn-I regions facilitated by 461 the built-in potential, we compared the transient absorption spectra with and without bias under 462 the same experimental setup. We used pump photons of a short wavelength of 610 nm 463 (Supplementary Fig. 36), with a pump fluence of 100 nJ·cm<sup>-2</sup>, to full excite both Bi/Sn-I and Sn-I regions. The GSB signals in the Bi-doped polycrystalline thin films were much weaker 464 465 than those in superlattices, due to the relatively poor carrier properties. Furthermore, in the 466 Bi<sup>3+</sup>-doped polycrystalline thin films and Bi-free superlattices (Supplementary Fig. 35), neither GSB nor excited state absorption (ESA; corresponding to the absorption of a photon from a 467 lower excited state to a higher excited state of the system) signals showed noticeable intensity 468 changes when a bias was applied. However, in the Bi<sup>3+</sup>-alloyed superlattice (Fig. 5a), the GSB 469 470 signals increased and the ESA signals decreased substantially when a 10 V bias was applied.

471	At zero bias, the GSB peaks in $\mathrm{Bi}^{3+}$ -free superlattices were located at ~840 nm
472	(Supplementary Fig. 35b), corresponding to the larger bandgap (~1.47 eV, 843 nm) of Sn-I
473	regions. In contrast, the GSB peaks in $\mathrm{Bi}^{3+}$ -alloyed superlattices were mainly located at ~925
474	nm (Fig. 5a), corresponding to the smaller bandgap (~1.34 eV, 925 nm) of Bi/Sn-I regions.
475	Note that there were small broad peak shoulders at ~830 nm in the dashed green square (Fig.
476	5a), which should be from the larger bandgap of Sn-I regions. Note that the GSB peak (~925
477	nm) for Bi <sup>3+</sup> -alloyed superlattice ( $n=3$ ) was shorter in wavelength than that measured by PL
478	(~990 nm; Supplementary Fig. 23b), because of different sample platforms. In the transient
479	absorption measurements, the superlattice was peeled off from the substrate, and the lattice
480	strain was then fully released; however, in the PL measurements, the superlattice was still on
481	the epitaxial substrate, and therefore, the organic spacers were largely compressed, reducing
482	the superlattice bandgap (Fig. 3c and Supplementary Fig. 20). Therefore, at zero bias, the
483	transient absorption results were consistent with those PL results.
484	Under bias, only Bi <sup>3+</sup> -alloyed superlattices exhibited noticeable spectral changes compared
485	to those at zero bias (Fig. 5a and Supplementary Fig. 35). In general, the increased GSB signal
486	intensities reflect the reduced population of ground-state electrons in the valence band: the
487	higher the intensity (i.e., more negative the GSB peaks), the less the ground-state electrons in
488	the valence band (i.e., the more electrons in conduction band). Therefore, the increased GSB
489	signal intensities in Bi3+-alloyed superlattices under bias revealed a reduced number of
490	electrons in the valence band. Because the excitation conditions for 0 V and 10 V measurements
491	were the same (pump photons of 610 nm; pump fluence of 100 nJ $\cdot$ cm <sup>-2</sup> ), the reduced number

492 of electrons in the valence band was not from a stronger excitation. Therefore, we infer that the

493 number of electrons relaxing from the conduction band to the valence band after excitation was494 reduced.

495 We measured the hot electron lifetime in all samples under bias (Supplementary Fig. 38) 496 and confirmed them to be close to those at zero bias (Supplementary Fig. 37). Then those 497 reduced number of electrons relaxing from the conduction band to the valence band after 498 excitation must have transported to other adjacent layers. The direction of the electrical field 499 determines that the electrons could not transport to the bottom ITO contact (Supplementary 500 Fig. 34). In this case, those reduced electrons could only transport to either the Sn-I regions or 501 the ICBA ETL layer. In the Bi<sup>3+</sup>-doped polycrystalline thin-film, the GSB signals did not 502 increase obviously, suggesting that the 10 V electrical field was not sufficient to drive electrons 503 to overcome the interfacial barrier from the Bi/Sn-I region to the ICBA ETL (Fig. 4c). As a 504 result, the only possibility was that those reduced electrons had transported to the Sn-I regions. 505 Considering the even higher energy barrier between the CBM of Bi/Sn-I regions and that of 506 Sn-I regions, the transport process could only be accomplished during the relaxation of hot 507 electrons, supporting the intra-band relaxation mechanism.

We use a simplified physical picture to better describe this process: Without a bias, the probe has initially detected 100 electrons in the valence band of Bi/Sn-I regions (Supplementary Fig. 36a). Then, the pump excited 50 electrons into the conduction band of Bi/Sn-I regions (Supplementary Fig. 36b). Those excited electrons will relax; however, they can only go to the CBM of Bi/Sn-I regions but not the Sn-I regions or ICBA because of the high-energy barriers. Therefore, when the probe detects the ground state again, some of the excited electrons may be still under relaxation, or at the CBM, or already relaxed from the

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515 CBM to the valence band (Supplementary Fig. 36c). Accordingly, the probe will detect, e.g., 516 75 electrons in the valence band. The GSB signal intensity (e.g., -25) corresponds to the 517 reduced 25 electrons compared to the original 100 electrons (Supplementary Fig. 36d).

518 With a bias, after the excitation, parts of the hot electrons can relax to the CBM in Sn-I regions (i.e., intra-band relaxation), because most of the hot electrons may already stay higher 519 520 than the CBM of Sn-I and the atomic-scale diffusion length makes this intra-band relaxation 521 efficient. However, those excited electrons are still not possible to travel to the ICBA because 522 that requires a much longer diffusion length, as evidenced by the fact that there is almost no 523 change in the transient absorption spectra for the Bi<sup>3+</sup>-doped polycrystalline device with and without the bias (Supplementary Fig. 35a). Note that even though the Bi/Sn-I regions and the 524 525 ICBA are in direct contact, the contact area is relatively small and the carriers have to diffuse 526 through the entire thickness of the superlattice (a few hundreds of nanometers) along the c527 direction to access the ICBA. In contrast, the carriers in the Bi/Sn-I regions have to diffuse only the width of the Bi/Sn-I regions (~0.6 nm) to access the Sn-I regions. Therefore, when the 528 529 probe detects the valence band again, besides those excited electrons that are still during 530 relaxation, at the CBM, or have already relaxed from the CBM to the valence band, there are 531 also electrons relaxing to Sn-I regions. Accordingly, the probe will detect less than 75 electrons (e.g., 65 electrons) in the valence band. Those 10 electrons moved from the Bi/Sn-I region to 532 the Sn-I region. As a result, the GSB signal intensity increases (more negative) to -35. 533

Besides the GSB signals, the decrease in ESA signal intensities in Bi<sup>3+</sup>-alloyed superlattice with a bias further supported the above mechanism. The changes in ESA signal intensities reflect the excited electron population that is excited further: the higher the intensity, the more 537 the excited electrons get excited further (Supplementary Fig. 36d). The decrease in ESA signals 538 in Bi<sup>3+</sup>-alloyed superlattices with a bias was due to a reduced number of hot electrons in the 539 conduction band. Because of the same excitation setup and similar hot electron lifetimes for 0 540 V and 10 V measurements (Supplementary Fig. 37c and Supplementary Fig. 38c), the 541 obviously reduced hot electron population was not from a weaker excitation or more rapid 542 relaxation but from additional relaxation routes. Because the ESA signals only refer to hot 543 electrons in excited-states with short lifetimes, it was impossible for them to transport for long-544 distances. Therefore, we concluded that they could only relax to Sn-I regions due to the atomic-545 scale diffusion distance. The only two other layers contacting with Bi/Sn-I regions were ITO and ICBA, which had relatively long diffusion distances. 546

We can also use a simplified physical picture to better explain this process. Without a bias, there are 100 electrons in the valence band in Bi/Sn-I regions. When the pump excitation is on, 50 electrons are excited. Then, those excited electrons will relax. When the probe detects again, 25 electrons have already relaxed to the valence band, 5 electrons stay at the CBM, and 20 electrons are still during relaxation. Specifically, among the remaining 20 hot electrons, 10 of them (i.e., 50% of the possibility) can further absorb the excitation, which yields an ESA signal of +10.

With a bias, the same 50 electrons are excited. Because the bias yields a higher GSB intensity through the intra-band relaxation (Fig. 5a), there will be only 15 electrons relaxing to the valence band of Bi/Sn-I regions and 10 electrons relaxing to Sn-I regions. The rest 25 electrons are in the conduction band of Bi/Sn-I regions: 5 stay at the CBM and 20 are still during relaxation, while part of the latter (e.g., 6 electrons) can also relax to Sn-I regions. Then, there are only 14 electrons during the relaxation in Bi/Sn-I regions. Therefore, under the same 560 50% possibility for them to be re-excited, the number of excited hot electrons is 7, which yields 561 an ESA signal of +7, smaller than the bias-free case (+10).

To summarize, the results of pump-probe ultrafast transient absorption spectra support the intra-band relaxation mechanism. Fundamental characterizations and device studies in this work have also confirmed the efficient carrier dynamics in the unprecedented low-dimensional perovskite superlattices, which can open a lot of exciting new opportunities in constructing high-performance devices using low-dimensional perovskite superlattices.

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Supplementary Fig. 1 | Schematics of different epitaxial models. Both models (a) and (b)
can be considered to contain an infinite *n*-value perovskite layer, which is thermodynamically

- 571 unstable. Only model (c) can form strong coherent metal-halide bonds between the substrate
- 572 and the epitaxial layer with thermodynamically stable small *n*-values.


574 Supplementary Fig. 2 | Detailed merging processes of epitaxial low-dimensional

575 **perovskites.** SEM images clearly show that the initial crisscross crystals gradually expand and

576 contact each other to form a completely merged thin film in the end.



578 Supplementary Fig. 3 | Epitaxial growth of low-dimensional perovskites on different 3D

**perovskite substrates.** Similar crisscross crystal morphology can be observed.



Supplementary Fig. 4 | Studies of the precursors' *n*-purity. (a) Optical images showing the as-synthesized low-dimensional perovskites with different *n* values. Each has a flake morphology. (b) Distinct PL signals from those crystals suggesting that their *n* values are highly pure. Polycrystalline thin films fabricated by the as-prepared precursors exhibit similar behaviors, as shown by (c) UV-vis and (b) PL measurements, confirming that the as-prepared precursor yields low-dimensional perovskites with highly pure *n* values.



Supplementary Fig. 5 | Fabrication of superlattices on commercially available BaF<sub>2</sub> 588 589 substrates. Optical images show the commercially available  $BaF_2$  (100) substrate before and after the superlattice growth (top panels). SEM images show the detailed growth steps: an 590 591 epitaxial MAPb<sub>0.5</sub>Sn<sub>0.5</sub>Br<sub>3</sub> layer is grown on the BaF<sub>2</sub> first; then, the superlattice layer is grown on the MAPb<sub>0.5</sub>Sn<sub>0.5</sub>Br<sub>3</sub> layer, showing a similar cross-hatched crystal morphology (middle 592 593 panels). Grazing-Incidence Wide-Angle X-ray Scattering mapping results show the crystal 594 orientations of the MAPb<sub>0.5</sub>Sn<sub>0.5</sub>Br<sub>3</sub> and superlattice. The superlattice exhibits clear in-plane orientations. 595



Supplementary Fig. 6 | Mapping of the *d*-spacing. (a) The extracted linear *d*-spacing curves 598 from Fig. 1b. Along the *b* direction, the *d*-spacing of the epitaxial layer equals to that of the 599 600 substrate. However, along the *a* direction, the *d*-spacing of the epitaxial layer is two times that 601 of the substrate. (b) Detailed d-spacing mapping from both a-c and b-c planes. In the b direction, the lattice constant of the Sn-I slab (~6.04 Å when conventionally grown, as calculated from 602 603 XRD) is ~5.96 Å, yielding 1.32 % strain. In the *a* direction, the *d*-spacing is ~11.92 Å, 604 containing one Sn-I slab (~6.04 Å when conventionally grown) and one organic spacer (~7.00 605 Å when conventionally grown, as calculated from XRD), corresponding to an overall compressive strain of 8.59%, which matches to the XRD results perfectly<sup>29</sup>. 606



608 Supplementary Fig. 7 | Cross-sectional high-resolution STEM image of a polycrystalline 609 film. It is clear that grain misorientations and boundaries exist along the thin-film thickness 610 direction, indicating strong barriers for carrier transport in common devices with top and 611 bottom contacts.



Supplementary Fig. 8 | Grazing-Incidence Wide-Angle X-ray Scattering mapping of 613 superlattices and polycrystalline thin films. (a) The epitaxial superlattices exhibit sharp and 614 discrete Bragg spots that almost only appear along the xy and z directions. Specifically, periodic 615 616 Bragg spots only appear along the xy axis in superlattices, which reveal that the inorganic 617 slab/organic spacer quantum wells are perpendicular to the xy directions (i.e., the substrate surface) and parallel to the z direction<sup>2, 21</sup>, confirming their vertical out-of-plane orientations. 618 619 In contrast, the random arc-like Bragg signals in polycrystalline thin films illustrate the random orientations of the crystal domains. (b) The 1D profiles extracted from a (top panel) match the 620 XRD results from  $\theta$  values in Fig. 3a ( $Q = \frac{2\pi}{\theta}$ ; bottom panel), further confirming the vertical 621 622 orientation of the superlattices. The peak splitting in the 1D profile of n=1 superlattice might 623 come from the veined surface of the sample, where strong lattice strain generates lattice dislocations and a rugged surface (Fig. 3b insets). 624



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626 Supplementary Fig. 9 | Schematics of polarized photocurrent measurements. The as-627 formed superlattice film contains a matrix-like structure, with two perpendicular crystals in 628 two different orientations, corresponding to a 90° period for the polarized photocurrent. In 629 contrast, the conventionally grown single crystal shows a 180° period due to its typical two-630 dimensional orientation.



632 Supplementary Fig. 10 | Orientation-dependent transient photovoltage measurements. (a) 633 Schematics showing three Au electrode pairs on top of an epitaxial low-dimensional perovskite superlattice. The 0° and 90° are considered to be the same because the superlattice is formed 634 635 by two perpendicular crystal plates, which exhibit a relatively long carrier lifetime. The 45° 636 experiences organic barriers, leading to a relatively short carrier lifetime. (b) Schematics showing three Au electrode pairs on the side surface of a conventionally grown low-637 638 dimensional perovskite single crystal. The conventionally grown single crystals are relatively thin due to their intrinsic 2D characteristics. Therefore, a long-time is needed to grow such 639 640 crystals so that the *a*-direction is thick enough for depositing electrodes on the side surface. 641 The 0° exhibits the longest carrier lifetime due to the absence of organic barriers. In contrast, the 90° exhibits the shortest carrier lifetime, while the 45° condition shows a lifetime in 642 between. (c) Representative raw data for samples with different orientation angles in Fig. 1d. 643 644 The carrier lifetime was obtained by exponential fitting of the decay curves. The carrier lifetime 645 is the interception between the slope of the decay curve and the decayed background.



- 647 Supplementary Fig. 11 | SEM images of polycrystalline thin films. Grain misorientations
- 648 and boundaries are numerous, suggesting strong energy barriers in every direction.









658 **Supplementary Fig. 13** | **Fabrication processes for** *in-situ* **superlattice devices.** The 659 schematics show detailed steps for fabricating *in-situ* superlattice devices with fully strained 660 superlattice perovskites in this work. Deposition of the ETL and top electrode follows the 661 growth of superlattice.



Supplementary Fig. 14 | Configuration of *in-situ* fabricated devices. (a) An optical image 663 664 of the pre-patterned polyimide mask with deposited Au and PTAA layers. (b) Schematic cross-665 section of the device (top panel). A pre-pattern polyimide (PI) is deposited with layers of Au and PTAA and used as the growth mask and the bottom contact. A thin epitaxial layer of 666 667 substrate is grown first to facilitate the growth of strained low-dimensional perovskite superlattice. The top and bottom electrodes do not have the same size, where the calculated 668 overlapped area (highlighted in orange) between the top and bottom electrodes is around 55% 669 670 of the entire area, which sacrifices the achieveable power conversion efficiency (bottom panel).



672 Supplementary Fig. 15 | Imperfect merging in the superlattice. (a) An SEM image of a 673 superlattice that is intentionally broken to investigate the merging process. The merged film, 674 albeit with a flat surface, may still bury invisible crystal boundaries. Structural defects are from 675 the imperfect crystal merging because of the large lattice mismatch between the substrate and the organic spacer in the epitaxial layer. (b) Schematics showing the merging process with 676 those crisscross thin crystal plates. The perfect merging, which requires the lattice orientation 677 678 to be matched in both a and b directions, is impractical due to the existence of both organic 679 spacers and inorganic slabs. The lattice misorientation between the organic spacers and 680 inorganic slabs is impossible to avoid in practice, resulting in merging defects.





683 Supplementary Fig. 16 | Schematic models of the epitaxial lattice strain. Computational results show the lattice parameters from optimized stable crystal structures. In the 684 conventionally grown Ruddlesden-Popper structure, the length of the Sn-I bond adjacent to the 685 organic spacer is ~0.302 nm, and the distance between two I atoms is ~0.700 nm, which 686 687 contains one organic spacer. In the superlattice, the length of the Sn-I bond adjacent to the organic spacer is ~0.297 nm, and the distance between two I atoms is ~0.598 nm, which 688 689 contains one organic spacer. The substrate has a Pb/Sn-Br bond of ~0.298 nm. Due to the 690 epitaxy, the superlattice is not the Ruddlesden-Popper structure anymore.





Supplementary Fig. 17 | Fourier-transform infrared spectroscopy characterizations. Both 692 693 superlattice and conventionally grown single crystals have been characterized. The results 694 show that the peaks in the superlattice shift apparently to higher wavenumbers, indicating the 695 vibration frequencies of the organic bonds in the superlattice are enhanced, which is from the 696 compressed organic spacers in the superlattice. To verify the observations, the Fourier-697 transform infrared spectroscopy has been simulated by only tunning the organic spacer from 698 the original (conventionally grown) to the compressed (superlattice) states. In the 699 computational results, the as-modeled superlattice exhibits clear peak shifting to higher 700 wavenumbers than the conventionally grown structure, which is similar to the experimental 701 measurement results, confirming that the compressed bonds in the organic spacer of the superlattice are the reason for the enhanced vibration frequency. 702



704Supplementary Fig. 18 | A summary of degradation of superlattices with different n-705values. (a) The degradation of superlattices is found to be highly related to the n-values. A706higher n-value exhibits higher stability. (b) Schematics show the epitaxial superlattices with707different n-values. If the volume ratio of the inorganic slabs is higher, the inorganic slabs are708more resistant to the lattice strain applied from the compressed organic spacers.





Supplementary Fig. 19 | Degradation in the superlattice. (a) Optical images showing clear changes in the morphology and color from the fresh to the degraded superlattices, where the degraded samples show obviously amorphous structures. (b) Kelvin probe force microscopy measurements confirming that the work function decreases enormously in the degraded sample, suggesting more insulating properties. Additionally, the larger variations in the measured voltages of the degraded sample than those of the fresh sample also indicate that the surface uniformity has been largely damaged by the degradation.





Supplementary Fig. 20 | Bandgaps for conventionally grown and superlattice lowdimensional Sn perovskites. Those values are from UV-Vis measurements under the reflection mode. The superlattices generally exhibit a smaller bandgap than the conventionally grown single crystals. As n increases, the bandgap also becomes smaller due to the reduced quantum confinement from the organic spacers. An extreme case is that when n equals to infinity, the low-dimensional perovskites become 3D perovskites.





725Supplementary Fig. 21 | Simulated unit cell of the  $BA_2MA_2Sn_3I_{10}$  (n = 3) superlattice. One726unit cell has been modeled to represent the overall structure due to the limited computational727resource available. Because only six  $Sn^{2+}$  ions are included in the modeling, the minimal  $Bi^{3+}$ 728percentage in the alloyed unit cell is 16.7%, which results from the replacement of one  $Sn^{2+}$ 729ion from the original six  $Sn^{2+}$  ions.



**Supplementary Fig. 22** | **Total energy calculations with Bi**<sup>3+</sup> **alloying.** (**a**) The unit cell structure for the BA<sub>2</sub>MA<sub>2</sub>Sn<sub>3</sub>I<sub>10</sub> superlattice before Bi<sup>3+</sup> alloying. To simplify the modeling, the lattice strain from the organic spacers is only applied from the left side. Sn atoms at different sites are marked with numbers from 1 to 6, which are replaced by the Bi<sup>3+</sup> to form six different structures. (**b**) The total energy with the different sites (from 1 to 6) of Sn<sup>2+</sup> to be replaced by Bi<sup>3+</sup>. When the Bi<sup>3+</sup> is set to be at sites 3 or 6, the unit cell exhibits the smallest total energy, indicating the most stable structure.



Supplementary Fig. 23 | XRD and PL characterizations of the Bi<sup>3+</sup> alloyed superlattice. 740 (a) XRD results show that there is no noticeable peak shifting after 10% Bi<sup>3+</sup> alloying, and the 741 742 superlattice structure also does not change because it is anchored by the substrate (left). After 743 10 days, the structure of the Bi<sup>3+</sup> alloyed superlattices is still stable, but the structure of the  $Bi^{3+}$ -free superlattices degrade obviously (right). (b) PL results show that the  $Bi^{3+}$  alloying 744 decreases the bandgap (from a radiative band structure; red curve) compared with Bi<sup>3+</sup>-free 745 superlattices (black curve). Additionally, Bi<sup>3+</sup> alloying forms the band tail structure (from a 746 non-radiative trap state; light brown curve) at different areas on the same sample (left). There 747 has been a substantial decrease in the PL intensity of the Bi<sup>3+</sup>-free superlattices (black curve) 748 but no noticeable change in the Bi<sup>3+</sup> alloyed superlattices (red curve) after 10 days (right). 749



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Supplementary Fig. 24 | Calculated electronic structures of the Bi<sup>3+</sup> alloyed BA<sub>2</sub>MA<sub>2</sub>Sn<sub>3</sub>I<sub>10</sub> superlattice. Bi<sup>3+</sup> alloying vastly decreases the CBM position, resulting in a smaller bandgap. (a) The density of states (DOS) plot of the Bi/Sn-I region in Fig. 4a. (b) The DOS plot of the Sn-I region in Fig. 4a. The CBM position in **a** has been noticeably decreased compared with **b**, indicating that Bi/Sn-I region exhibits a smaller bandgap, which is mainly because of the energy contribution from the *p* orbitals of the Bi<sup>3+</sup> ions.



Supplementary Fig. 25 | Calculated electronic structures of the  $BA_2MA_2Sn_3I_{10}$ superlattice when  $Bi^{3+}$  replaces  $Sn^{2+}$  at different sites. The  $Bi^{3+}$  can influence the electronic structure of surrounding  $Sn^{2+}$  by replacing the original Sn-I-Sn with the Sn-I-Bi. The DOS plots of the six ions in the unit cell are shown. Those ions closer to the  $Bi^{3+}$  have a smaller bandgap, which is caused by the decreased CBM position from the *p* orbitals of the  $Bi^{3+}$  ions.



764Supplementary Fig. 26 | X-ray photoelectron spectroscopy measurements of  $Bi^{3+}$  alloyed765superlattice. Obvious peaks in (a) from the Bi  $4f_{5/2}$  and Bi  $4f_{7/2}$  are evident in the Bi $^{3+}$  alloyed766 $BA_2MA_2Sn_3I_{10}$  superlattice. However, the Bi $^{3+}$ -free  $BA_2MA_2Sn_3I_{10}$  superlattice in (b) does not767have any noticeable peaks associated with Bi in this range of binding energy.



770Supplementary Fig. 27 | Textured surfaces and light-trapping properties of the771superlattice. (a) SEM images showing the textured surface of the epitaxial  $BA_2MA_4Sn_5I_{16}$ 772layer grown on different crystal facets of the 3D perovskite substrate<sup>15, 36</sup>. (b) Reflection773measurement results showing that the optimized tilting angle of the microstructures is 60° (left),774which gives the smallest reflection, as evidenced by the optical images (right).



Supplementary Fig. 28 | Band structures of the ICBA layer. (a) UV-Vis measurements of
the ICBA layer under the absorption mode. The bandgap is determined by the cutoff from the
dash lines. (b) UPS measurements of the ICBA layer. The CBM is calculated by the cutoff
from the dash lines in both high and low binding energy regions.



Supplementary Fig. 29 | Photovoltaic performance certificate from Newport. A beyond-Shockley-Queisser-limit  $V_{OC}$  of 0.967 V has been recorded with a bandgap of 1.042 eV in a single-junction device. (a) The detailed report from Newport, where the Sn-based 2D perovskite (n = 5) serves as the absorber layer with an Au/PTAA/perovskite/ICBA/ITO structure. The certified  $V_{OC}$  is 0.967 V under the quasi-steady-state condition. (b) The quantum efficiency plot of the certified device. The carrier collection cutoff (~1190 nm) in the plot indicates that the device bandgap is 1.042 eV. However, according to the Shockley-Queisser-

189 limit, the theoretical maximal  $V_{OC}$  for such a photovoltaic is 0.802 V. (c) The I-V curve of the 190 certified device under the quasi-steady-state, showing negligible hysteresis because the high 191 quality structure of the superlattice suppresses ion migration, reduces internal charge 192 recombination, and eliminates accumulation of ions.



**Supplementary Fig. 30** | **Stability studies of strain-free superlattices.** (a) In-plane XRD characterizations showing that the transferred strain-free superlattice can maintain an intact structure without degradation for at least one month. (b) PL and (c) time-resolved PL measurements confirming that carrier properties of the transferred strain-free superlattice do not degrade for at least one month. (d) Atomic force microscopy and Kelvin probe force microscopy measurements also indicate that the transferred strain-free superlattice does not experience morphological or electrical degradation.



802 Supplementary Fig. 31 | Stability studies of strain-free superlattice solar cells. (a) J-V 803 measurements under 1000-hour continuous illumination showing that the strain-free superlattice solar cell exhibit a similar shape, indicating no obvious efficiency drop. The device 804 805 is based on an ITO/SnO<sub>2</sub>/BA<sub>2</sub>SnI<sub>4</sub> superlattice/Spiro/Au structure, which might not give an 806 optimal efficiency but is appropriate for studying the device stability. (b) Extracted short-807 circuit current density, fill factor, and  $V_{OC}$  from curves in **a**, confirming that the device decay 808 is negligible. Those results suggest that the strain-free superlattice structure itself is stable 809 because they are composed of stable low-dimensional perovskites.









Supplementary Fig. 33 | Schematics of carrier transport in the superlattice photovoltaic 818 819 device. The patterned polyimide serves as the mask for epitaxial growth. A thin layer of 820 MAPb<sub>0.5</sub>Sn<sub>0.5</sub>Br<sub>3</sub> (~200 nm) is first epitaxially grown on the MAPb<sub>0.5</sub>Sn<sub>0.5</sub>Br<sub>3</sub> bulk substrate to 821 provide uniform strain to the low-dimensional perovskites. The strained low-dimensional perovskite layer exhibits a vertical alignment to form a superlattice. In particular, the strain-822 823 induced Bi<sup>3+</sup> alloying creates two different band structures in the inorganic slabs (Bi/Sn-I region and Sn-I region), where the Bi/Sn-I shows a smaller bandgap with a lowered CBM. Due 824 825 to the energy barrier and long diffusion length between the Bi/Sn-I and the ETL layer, electrons 826 are not likely to transport directly from the Bi/Sn-I to the ETL (white arrows). Instead, electrons 827 are excited to high-energy states and diffuse to the Sn-I by intra-band relaxation and then transfer to the ETL (red arrows). Due to the energy barrier between the superlattice and the 828 829 MAPb<sub>0.5</sub>Sn<sub>0.5</sub>Br<sub>3</sub> layer, holes are likely to accumulate/recombine at their interface to form band 830 tail states. The holes can still be extracted by the HTL to close the charge flow loop.



Supplementary Fig. 34 | Fabrication processes of devices for transient absorption characterizations. The detailed schematics are for (a) superlattice devices and (b) polycrystalline devices. A bias can be applied to the perovskites and ICBA ETL by the two ITO electrodes, mimicking the built-in-potential in solar cells. A transparent double-sided polypropylene tape is used to prevent any current injection to the device, mimicking the opencircuit condition in solar cells.



839 Supplementary Fig. 35 | Measurements of transient absorption spectra. Transient 840 absorption spectra are measured for (a)  $Bi^{3+}$ -doped  $BA_2MA_2Sn_3I_{10}$  polycrystalline thin film, 841 and (b)  $Bi^{3+}$ -free  $BA_2MA_2Sn_3I_{10}$  superlattice. No obvious changes in GSB or ESA signals can 842 be noticed with and without a 10 V bias, indicating the applied bias doe not influence the hot 843 carrier dynamics in those samples.





845 Supplementary Fig. 36 | Processes of transient absorption measurements. (a) Probe pulse 846 measurement, where the absorbance of the perovskite is proportional to the number of electrons 847 in the valence band. (b) Pump pulse measurement, where the photo excitation happens. (c) 848 Delay process, where a short time duration allows a portion of hot electrons to relax to the CBM and recombine with holes in the valence band. (d) Probe pulse measurement, where the 849 850 absorbance of the perovskite will be measured again. The change in the number of electrons in 851 the valence band leads to the GSB signal, while the change in the number of electrons in the conduction band results in the ESA signal. 852






864 Supplementary Fig. 38 | Measurements of hot carrier relaxation lifetimes with bias. The 865 hot carrier relaxation lifetime is measured by transient absorption for (a)  $Bi^{3+}$ -alloyed 866  $BA_2MA_2Sn_3I_{10}$  superlattice, (b)  $Bi^{3+}$ -free  $BA_2MA_2Sn_3I_{10}$  superlattice, and (c)  $Bi^{3+}$ -doped 867  $BA_2MA_2Sn_3I_{10}$  polycrystalline thin film with a 10 V bias. All of these lifetimes show negligible 868 changes from those without a bias. The results exclude the influence of the applied bias on the 869 hot carrier lifetimes.

Structure	а	b	c
MAPbBr <sub>3</sub>	~0.598 nm	~0.598 nm	~0.598 nm
BA <sub>2</sub> Snl <sub>4</sub>	~1.304 nm	~0.604 nm	~0.604 nm
MASnBr <sub>3</sub>	~0.594 nm	~0.594 nm	~0.594 nm
$MAPb_{0.5}Sn_{0.5}Br_3$	~0.596 nm	~0.596 nm	~0.596 nm
Superlattice BA <sub>2</sub> SnI <sub>4</sub>	~1.192 nm	~0.596 nm	~0.610 nm
BA spacer	~0.700 nm		

Structure	Lattice strain	Lattice strain
Superlattice BA <sub>2</sub> SnI <sub>4</sub> (inorganic slab)	~-1.66% along the <i>a</i> direction ~-1.32% along the <i>b</i> direction	~0.99% along the c direction
Superlattice BA <sub>2</sub> SnI <sub>4</sub> (organic spacer)	~-14.60%	-
Superlattice BA <sub>2</sub> SnI <sub>4</sub> (overall)	~-8.59%	~0.99%

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## 871 Supplementary Table 1. Summarized lattice parameters and strains in the epitaxial

## 872 growth processes. Those values are calculated from STEM and XRD results. Negative means

873 compressive strain, and positive means tensile strain.

Material	VBM	Bandgap	СВМ
ICBA	-5.96 eV	2.35 eV	-3.61 eV
PTAA	-5.02 eV	1	1
MAPb <sub>0.5</sub> Sn <sub>0.5</sub> Br <sub>3</sub>	-5.45 eV	2.12 eV	-3.33 eV
BA <sub>2</sub> MA <sub>4</sub> Sn <sub>5</sub> I <sub>16</sub>	-4.76 eV	1.26 eV	-3.50 eV
10% Bi-BA <sub>2</sub> MA <sub>4</sub> Sn <sub>5</sub> I <sub>16</sub>	-4.76 eV	1.04 eV	-3.72 eV

876 Supplementary Table 2. Summarized band structures of the materials used in the
877 certified photovoltaic device. Those values are calculated from UV-Vis and UPS
878 measurements.

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