1   Stable and low photovoltage loss perovskite solar cells by multifunctional

2   passivation

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Abstract: Metal halide perovskite solar cells (PSCs) have demonstrated high power conversion efficiency (PCE), while further efficiency enhancement requires reducing bandgap-voltage offset (W_{OC}) and non-radiative recombination photovoltage loss ($\Delta V_{OC,nr}$). Here, we report an effective approach in reducing the photovoltage loss through the simultaneous (a) internal bulk defects and (b) dimensionally graded 2D perovskite interface defects passivation. Through this Dimensionally Graded Perovskite Formation (DGPF) approach, an open-circuit voltage (V_{OC}) of 1.24 V was obtained with a champion PCE of 21.54% in a 1.63 electron volts (eV) perovskite system (maximum V_{OC}=1.25 V, W_{OC}=0.38 V, and $\Delta V_{OC,nr}$=0.10 V); we further decreased W_{OC} to 0.326 V in a 1.53 eV perovskite system with a V_{OC} of 1.21 V and a PCE of 23.78% (certified 23.09%). This approach is equally effective in achieving low W_{OC} ($\Delta V_{OC,nr}$) in 1.56 eV and 1.73 eV PSC systems, and further leads to significantly improved operational stability of PSCs.

Introduction

Perovskite solar cells (PSCs) based on three-dimensional (3D) perovskite absorbers have achieved rapid progress with power conversion efficiency (PCE) of over 25%, due to the outstanding optoelectronic properties of 3D perovskites. Nevertheless, their poor stability nature, particularly the susceptibility to humid environments, lack of thermal stability, and light-soaking degradation, become a major shortcoming that limits their further practical application.

As PSCs' band gap-voltage offset (W_{OC}) is still higher than GaAs (W_{OC}~0.3 V) cells [1], reducing the W_{OC} and pushing the PSCs' V_{OC} towards the Schottky-Queisser V_{OC} limit (radiative recombination loss only) is of great significance in boosting the PCE as well as understanding the fundamental science [2, 3, 4, 5, 6]. Several studies have shown that non-radiative recombination via defects at the interfaces between perovskite and charge transport layers are the main sources of voltage losses for PSCs[7, 8, 9]. Strategies such as surface passivation or processing additives have been explored to minimize the non-radiative recombination losses at interfaces and thus to

76 improve the V_{OC} of devices[10, 11]. For example, surfaces and grain boundaries with

77 potassium passivation was shown to enable substantial mitigation of non-radiative

78 recombination losses ($\Delta V_{OC,\text{nr}}$), pushing the V_{OC} up to 1.17 V with a low W_{OC} of 0.39

79 V ($\Delta V_{OC,\text{nr}}$ = 0.11V) for a 1.56-eV-bandgap 3D perovskite system. However, there are

80 still substantial non-radiative losses causing from trap states within the perovskite

81 bulk film, which limits the performance and stability of perovskite devices[12]. In

82 addition, the energy level alignment at the interface is also a key factor for

83 minimizing interfacial non-radiative recombination, which requires careful interface

84 design[13]. Thus, simultaneous interface and bulk trap passivation strategy as well as

85 interface engineering are required to further reach the full thermodynamic potential of

86 V_{OC}.

87   In this work, we introduced a multifunctional (bulk and interface) 2D perovskite

88 passivation approach and graded interface design to significantly reduce PSC

89 photovoltage loss and enhance device stability. N-butylammonium bromide (BABr)

90 was first coated on top of the 3D perovskite film, and through thermal driving, we

91 simultaneously achieved relatively uniform distribution of self-passivated 2D/3D

92 perovskites in the bulk, covered by graded mixed dimensional, wider bandgap 2D

93 perovskite layers. We name it as Dimensionally Graded Perovskite Formation (DGPF)

94 approach. This multifunctional approach effectively suppresses the non-radiative

95 recombination loss in both the bulk and the interface of perovskite. Via this DGPF

96 technique, we demonstrate a hysteresis-free maximum PCE of 21.54% with a high

97 V_{OC} of 1.24 V in a 1.63 eV perovskite system, and the W_{OC} is only 0.39 V, equivalent

98 to non-radiative recombination V_{OC} loss ($\Delta V_{OC,\text{nr}}$) of only 0.11 V. Particularly,

99 minimum W_{OC} of 0.38 V and $\Delta V_{OC,\text{nr}}$ of 0.10 V was achieved in a 20.15% PCE device.

100 We further decrease the W_{OC} as low as 0.326 V in a ~1.53 eV perovskite system

101 ($\Delta V_{OC,\text{nr}}$ = 74 mV), with a maximum V_{OC} of 1.21 V and champion PCE of 23.78%

102 (certified PCE of 23.09%). The DGPF approach is also validated by examining hybrid

103 PSCs with bandgaps of 1.56 eV and 1.73 eV, where very low W_{OC} ($\Delta V_{OC,\text{nr}}$) and high

104 V_{OC} were both achieved. At the same time, the 2D perovskite components in the bulk

105 and at the interface provide superb stability under illumination, ensuring the DGPF

106   device can maintain 91% of its initial efficiency over 500 h under 1-sun illumination

107   at MPP condition.

108   Fig. 1a shows the schematic illustration of our DGPF method, and Fig. 1b shows

109   the cross-sectional high-resolution transmission electron microscope (HRTEM) of the

110   DGPF perovskite film deposited on the SnO_2-coated ITO substrate, which can verify

111   the homogeneity of 2D perovskite layer on the top of 3D perovskite films [14]. The 3D

112   perovskite films with a quaternary-cation of RbCsMAFA was formed by using the

113   antisolvent-assisted one-step method [15], which has demonstrated state-of-the-art

114   device performances in several studies from EPFL team[15, 16, 17]. The quaternary-cation

115   perovskite system has shown not only high efficiency, but also higher V_{OC} (1.16-1.18

116   V) than ternary-cation (~1.13 V) counterpart (both are ~1.63 eV bandgap) [15, 16, 17]. The

117   detailed fabrication method of the device is given in the Experimental Section. Here,

118   to   form   a   mixed   2D/3D   perovskite   heterojunction   films,   long-chain

119   n-Butylammonium bromide (BABr) molecules were first dissolved in isopropyl

120   alcohol (IPA) with different concentrations, and then directly spin-coated to form a

121   thin film on top of the as-prepared 3D RbCsMAFA perovskite films, which was

122   followed by thermal annealing at 100℃ for 10 min. This approach leads to perovskite

123   vertical composition distribution evidenced below.

124   To investigate the distribution of ions inside the perovskite films after introducing

125   BABr, we conducted time-of-flight secondary ion mass spectrometry (ToF–SIMS)

126   measurement on the DGPF perovskite films. ToF-SIMS depth profile shown in Fig.

127   1c reveals that a gradient distribution of BA^+ with the initial sputtering time, which

128   indicates the ultrathin 2D perovskite film was formed at the surface of 3D perovskite

129   layer. In the bulk (originally pure 3D) perovskite film, we now observe a relatively

130   uniform distribution of BA^+ with an over 2-orders lower intensity compared with the

131   BA^+ on the surface, indicating a clear diffusion process. Therefore, it is evident that

132   the bulk film contains both 3D and 2D perovskite with an increasing 2D concentration

133   towards the surface. Owing to the gradient distribution of BA^+, the layer number (n)

134   of the 2D perovskites might increase from the surface to the bulk, creating a tendency

135   of bandgap narrowing (as illustrated in Fig. 1a and Supplementary Fig. 10b).

136   Grazing-incidence wide-angle X-ray scattering (GIWAXS) technique was carried

137   out to study the crystal orientation of the control and mixed DGFP perovskite films [18].

138   The scattering patterns of perovskite films with various concentrations of BABr are

139   shown in Fig. 2a. The corresponding radial intensity profiles averaged over the whole

140   images are presented in Fig. 2b. The standard pure 3D perovskite film displays

141   uniform diffraction rings, indicating the formation of perovskite polycrystals with

142   randomly oriented cubic structure. For the perovskite films with the BABr

143   post-treatment, sharp diffraction peaks emerged at q = 0.32, 0.64, and 0.96 $Å^{-1}$ along

144   the q_z direction (Fig. 2c), which are indexed as (020), (040), (060) planes of layered

145   2D perovskite crystals parallel to the substrate with a layer spacing of ~20 $Å$ (n=2) [19].

146   The parallel 2D perovskite orientation is surprising, as it is commonly considered to

147   be unfavored for the overall vertical charge transport in solar cell devices. However,

148   the high efficiency PSC in this study indicates that the 2D perovskite layer with

149   relatively larger bandgap is thin enough for carrier transport, and can act as an

150   effective electron blocking layer to suppress the interfacial charge recombination. The

151   BABr GIWAXS peak appeared at q_z = 0.41 $Å^{-1}$ in the pure BABr film

152   (Supplementary Fig. 1a) and the excessive PbI_2 peak appeared at q_z = 0.92 $Å^{-1}$ in the

153   3D perovskite film were both absent, suggesting that 2D perovskite layers are

154   partially formed from the reaction of BABr with the excessive PbI_2. When the

155   concentration of BABr increases, the 2D perovskite peaks become more intensive, as

156   the higher order (080) peak appears with the 5 mg/ml BABr treatment.

157   To provide more detailed evidence of the graded 2D perovskite from the surface

158   to the bulk, we conducted GIWAXS analysis at different X-ray incident angles to

159   elucidate the vertical structure of the surface and internal perovskite layers with

160   depth-dependent characterization as shown in Supplementary Fig. 2. The structure

161   information of perovskite film surface was recorded at a small incident angle of 0.1˚,

162   which shows the formation of 2D perovskite layer with n=2 only. When the angle of

163   incidence was increased to 0.3˚, we can clearly observed some additional diffraction

164   peaks, which are assigned to be the (0k0) plane of 2D perovskite with n=3. With

165   increasing the incident angle and penetration depth, the diffraction peak intensity of

166   2D perovskite with n=2, 3 gradually increased. We can also clearly distinguish the

167   (222) plane of 2D perovskite with n=2, 3, and 4 at an incident angle of 1˚. Thus, the

168   depth-dependent GIWAXS results are in good agreement with our hypothesis of

169   graded top 2D perovskite layers with increased n values for top-down distribution. To

170   further evaluate the structural property of the DGPF perovskite films, we performed

171   high-resolution transmission electron microscope (HRTEM) measurement with

172   focused ion beam (FIB) lift-out technique shown in Supplementary Fig. 3, which can

173   offer the chance to probe the crystal structure throughout the perovskite film. Here,

174   we selected two regions (region 1 and 2), which correspond to the top surface and

175   bulk, respectively. The region 1 (top surface) shows lattice fringes with characteristic

176   d-spacing of 13 Å, which can be ascribed to 2D perovskite phases with n=1. At region

177   2 (bulk film), we can observe the characteristic d-spacing of 3D perovskite phase (3.2

178   Å). Besides, it is worth noting that 2D perovskite phases with n=2 and 3 were

179   embedded within 3D perovskite phases, which may probably located at the grain

180   boundary.

181   The influence of the annealing time on the perovskite film was also investigated,

182   as shown in Supplementary Fig. 1. The 2D perovskite signals remain almost the same

183   for the samples with and without annealing, whereas, the 3D perovskite signals

184   become stronger with longer annealing time. The diffraction peaks shift towards

185   larger q values, indicating a slight lattice contraction[20]. It is attributed to the

186   substitution of the relatively larger I^- ions with the smaller Br^- ions in 3D perovskite

187   crystals. The longer the annealing time, the more BABr diffused into the bulk film,

188   causing larger lattice contraction, consistent with the ToF-SIMS results. Therefore, as

189   illustrated in Fig. 2d, upon BABr post-treatment, BA^+ and Br^- ions tend to fill the

190   vacancies at grain boundaries of 3D perovskite due to the strong reactivity of

191   introduced BA^+ and Br^- ions with existed dangling bonds[21]. In this case, 2D

192   perovskite phases are most likely to form at the grain boundaries surrounding the 3D

193   perovskite phases. The 2D perovskite will heal and passivate the 3D perovskite

194   defects, significantly reduce the non-radiative recombination, which is in agreement

195   with the observed lower V_{OC} loss presented in the following.

196   Perovskite film morphology is another critical factor for photovoltaic
197 performance. Top-view scanning electron microscope (SEM) images and atomic force
198 microscopy (AFM) images of control and DGPF perovskite films are shown in Fig. 2e.
199 The morphology of the control RbCsMAFA perovskite film is uniform and compact
200 with well-crystallized grains, which is in good agreement with previous report [15].
201 With BABr treatment, an obvious grain coarsening process was observed, i.e., the
202 original small perovskite grains were merged into large ones via a thermodynamically
203 spontaneous Ostwald ripening process [22]. We expected that the BABr molecules
204 would gradually penetrate into the existing 3D perovskite crystalline structure,
205 resulting in the formation of thin 2D perovskite phases on the top and the bulk of
206 mixed 2D/3D perovskites film. When a low concentration of BABr solution was used
207 (1 mg/ml or 2 mg/ml), we observe both large and small grains. It is reasonable to
208 expect that in the low concentration cases, the amount of BABr is not enough for
209 recrystallizing all the small-grain-sized 3D perovskite crystals. With further increase
210 of the BABr concentration to 5 mg/ml, the surface morphology became smoother with
211 uniformly distributed grain sizes.

212   The photovoltaic devices were fabricated using Spiro-OMeTAD as hole selective
213 layer (HSL) and Au as counter electrode. The current density–voltage (J–V) curves of
214 the champion control and DGPF PSCs are shown in Fig. 3a. The control
215 RbCsMAFA-based planar PSC device shows a decent champion PCE of 19.61% with
216 a short-circuit current density (J_{SC}) of 22.25 mA cm^{-2}, a V_{OC} of 1.161 V, and a fill
217 factor (FF) of 75.92%. The V_{OC} and J_{SC} are very close to EPFL reports on mesoporous
218 PSCs, while the FF is lower (0.76 vs. 0.81). After BABr treatment, the DGPF PSC
219 exhibits clear performance enhancement, yields a champion PCE of 20.24% when
220 using 1 mg/ml BABr, and 21.54% when using 2 mg/ml BABr, with an impressive V_{OC}
221 of 1.24 V (Supplementary Fig. 4). We fabricated 20 devices in each condition, and the
222 detailed statistical analysis is summarized in Supplementary Table 4. The statistics of
223 two types of devices (control and DGPF PSCs @2 mg/ml BABr) is shown in
224 Supplementary Fig. 5, which indicates good reproducibility in DGPF PSCs with an
225 improved PCE of 20.38% (±0.38%) on average compares to 18.80% (±0.31%) in

226   control PSCs. A much enhanced average V_{OC} of 1.22 V (±0.02V) in the DGPF PSC,

227   compares to 1.15 V (±0.02V) in pure 3D PSCs, is the major factor contributing to the

228   overall efficiency enhancement. Considering the almost same optical bandgap for the

229   control and DGPF perovskite films, the driving force of high V_{OC} values with a small

230   W_{OC} for the DGPF PSCs are of great interest.

231   The external quantum efficiency (EQE) data of PSCs with different BABr

232   conditions are shown in Supplementary Fig. 4b. As expected, the EQE spectrum is

233   softly blue-shifted when incorporating BABr, which is very small and do not lead to

234   the J_{SC} reduction. We observed better photo response in the long wavelength range for

235   the devices treated with BABr solutions, which may originate from enhanced charge

236   transports [23]. For the RbCsMAFA system, when using the BABr solution with an

237   optimized concentration of 2 mg/ml, the 21.54% PCE cell achieved is also

238   hysteresis-free, and the stabilized PCE is 21.27%, as shown in Fig. 3a and

239   Supplementary Fig. 6. Here, we also compared some results of PSCs with over 21%

240   PCE, where the W_{OC} varies from 0.39 to 0.48 V, and our DGPF device demonstrated a

241   record V_{OC} among them (Supplementary Fig. 7 and Table 3)[15, 24].

242   To understand the fundamental of the high V_{OC} in these PSCs in a quantitative

243   manner, the accurate determination of perovskite bandgap is critical. As shown in

244   Supplementary Fig. 8, the determination of optical bandgaps was conducted in two

245   widely recognized methods: (a) Using the maximum point of the derivative of the

246   EQE spectra (i.e. dEQE/dE) [25], and (b) Tauc plot method) [26]. The E_g values from the

247   two methods agree very well.

248   We first exam the electroluminescence (EL) efficiency. The reciprocity relation

249   can describe the relationship between the photovoltaic quantum efficiency (EQE_{PV})

250   and the external quantum efficiency of the electroluminescence (EQE_{EL}), which can

251   be used to quantify the V_{OC} loss in photovoltaic devices [27]. According to Rau,

252    $\Phi_{EL}(E) = \varphi_{BB}(E)EQE_{PV}(E)\left[\exp\left(\frac{qV}{kT}\right) - 1\right]$, where $\varphi_{BB}(E)$ is the black body

253   emission flux density, the $\Phi_{EL}(E)$ is the EL spectral photon flux ($\Phi_{EL}(E) = $

254    $\frac{J_{inj}(V)}{q}EQE_{EL}(E)$), and $J_{inj}(V)$ is the injected current. As shown in Fig. 3b, the

extracted EQE_{PV} exhibited a nearly exact dependence on energy as the measured EQE_{PV}, implying the reciprocity relations hold. Herein, we identify the origins of increased open-circuit voltage in DGPF PSCs by quantifying the dominating recombination mechanisms. The first term $V_{OC,rad}$ describes the radiative limit of V_{OC}, which is determined by $V_{OC,rad} = \frac{kT}{q} \ln \left[\frac{J_{SC}}{\int_0^\infty EQE_{PV}(E)\varphi_{BB}(E)dE} + 1 \right]$ [6]. The calculated $V_{OC,rad}$ is 1.35 V for both reference control and DGPF perovskite devices, both with almost the same 1.63 eV bandgap [28]. Therefore, the difference in the non-radiative recombination losses is the source of V_{OC} enhancement. We then quantify the second term non-radiative recombination voltage loss ($\Delta V_{OC,nr}$), which in principle can be estimated from the measured EQE_{EL}, with the relationship of $\Delta V_{oc,nr} = V_{OC,rad} - V_{OC} = -\frac{kT}{q} \ln EQE_{EL}$. An EQE_{EL} of 0.85% was measured for a DGPF PSC device under LED mode with forward bias current density of 22.22 mA/cm^2 (Fig. 3c). This external EL quantum efficiency is very close that of the most efficient silicon solar cell (~0.5%)[29]. This is also one of the highest values obtained in PSCs. The 0.85% EQE_{EL} corresponds to a $\Delta V_{OC,nr}$ of 0.12 V [15, 30], which agree well with the device parameter (V_{OC} =1.23 V for the tested device). For the champion efficiency device with a V_{OC} of 1.24 V, the EQE_{EL} should be higher, and the $\Delta V_{OC,nr}$ will be 0.11 V. The maximum V_{OC} of 1.25 V with 20.15% PCE for the DGPF PSC device indicates a 100 mV $\Delta V_{OC,nr}$ (Supplementary Fig. 9). On the other hand, the control PSC has a V_{OC} of 1.16 V. Under the forward bias LED mode with the same injected current density of 22.22 mA/cm^2, the PSC delivers an EQE_{EL} of 0.065% (corresponding to $\Delta V_{OC,nr}$ of 0.19 V from the equation), which also agrees well with the device V_{OC} loss analysis. The extraordinarily low non-radiative recombination losses in DGPF PSCs are the dominating reason behind the high V_{OC} as well as the high efficiencies in these PSC devices. Generally, these non-radiative recombination losses arise from defects (charge carrier traps) either in the bulk photovoltaic materials or at the interfaces.

The ultraviolet photoelectron spectroscopy (UPS) on 3D perovskite films with different BABr concentrations are performed to understand electronic properties of

the films. Supplementary Fig. 10a shows the cutoff energy (E_{cutoff}) in high binding

energy region and valance band (VB) with respect to vacuum level derived from UPS

spectra. With the increase of BABr concentration, the E_{cutoff} shifts to higher binding

energy, indicating the ion-exchange induced 3D to 2D phase transition can reduce the

Fermi level of RbCsMAFA [19]. The valence band edges determined by the linear

portion in low binding energy region for 0-BABr, 1-BABr, 2-BABr, and 5-BABr are

located at 5.86, 5.80, 5.74, and, 5.70 eV, respectively. Here, to mimic a similar

situation, a thinner ~100 nm 3D perovskite films with and without BABr treatment

are used to enhance signal-noise-ratio. The absorption spectra of the thin control and

DGPF perovskite films are shown in Supplementary Fig. 11. It is noteworthy that the

absorption peak could be observed at 2.27, 2.05, and 1.81 eV, which are assigned to

2D perovskites with n=2, 3, and 4, respectively. As discussed above, the

depth-dependent GIWAXS data also confirmed this graded distribution. The top-down

structure information shows that the 2D perovskites with small n value (n=2) are

prone to be existed near the surface. Due to graded distribution of BA^+ in the 2D

perovskite region (Figure 1c), the energy diagram at the perovskite/HTL interface can

be estimated[31]. As shown in Supplementary Fig. 10b, the energy diagram of

perovskites with gradient energy structure distribution for the 2mg/ml BABr treated

case is depicted. Compare to pure 3D perovskite device, the graded 2D perovskites

lead to a graded energy level transition from bulk 3D perovskite to 2D perovskite. The

energy level shift is not linear, envisioned from BA^+ spatial distribution. We can

expect the energy level gradient is smooth close to bulk perovskite, but the gradient is

much faster when reaching the spiro-OMeTAD HTL side. Therefore, the

aforementioned graded 2D perovskite layer can be regarded as of the same function as

the graded window layer in traditional thin film solar cells, which provide a potential

barrier for the electrons [32]. The electrons moving towards perovskite top surface

(where the trap state density is higher than that in the bulk) will be reflected back

close to the interface. This energy level alignment thus will further eliminate the

surface recombination effectively. In the meantime, the mildly graded valance band

energy level alignment transition can also facilitate efficient hole transport from

314   perovskite to HTM.

315   Photoluminescence (PL) and time-resolved PL (TRPL) measurements were

316   conducted for the various perovskite films to examine the defect passivation effect

317   (Supplementary Fig. 12). For the DGPF perovskite films, in addition to a significant

318   PL intensity enhancement, we observed a slight blue-shift of the PL peaks, which

319   agree with the scenario of the Br⁻ substitution to I⁻, and the resulted shrinkage of the

320   3D crystal lattice. The carrier lifetime of control perovskite film was significantly

321   increased in the self-passivated DGPF perovskite films. All DGPF perovskite films

322   exhibit a long exponential PL decay tail with PL lifetimes above 1 μs (in particular, a

323   PL lifetime of 1.86 μs was obtained for 2-BABr sample), contrasting the shorter one

324   (0.76 μs) for the control perovskite film. This is consistent with the higher voltages

325   shown in Fig. 3c for DGPF perovskite devices, in which the defects were effectively

326   passivated[33]. Furthermore, we measure the external photoluminescence quantum

327   efficiency (PLQE) for the perovskite films with different contacts. The geometry of

328   the PL measurement is shown in Supplementary Fig. 13, in which the light excitation

329   either from top side or bottom sides. Here we used an incident laser with wavelength

330   of 485 nm, which has a penetration depth less than 100 nm according to Snell's law,

331   which implies that we can mainly collect the PL signal near the top surface of

332   perovskite film under the front excitation[34]. The PLQE of DGPF perovskite film

333   deposited on the glass reaches a value of 13.58%, whereas only 4.65% for control

334   perovskite film. When the presence of charge selective contacts (electrons or holes),

335   the PLQE values for both control and DGPF perovskite films decrease, which can be

336   ascribed to the quench effect and introduced non-radiative channels at the contact

337   interface[35]. We again observe that the DGPF approach enable a less notable reduction

338   in PLQE upon presence of selective contacts. In the case of light excitation from

339   either top or bottom, the higher PLQEs for the DGPF perovskite samples suggest that

340   optoelectronic properties of perovskite film as well as its related interfaces and

341   surfaces can be optimized via DGPF method.

342   Highly sensitive photothermal deflection spectroscopy (PDS) technique is

343   conducted to study the sub bandgap/trap state absorption and energetic disorder in

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these samples [36]. A decrease of sub-bandgap absorption determined by the PDS is clearly seen in the DGPF perovskite films, indicating reduced sub-bandgap states (trap states). The presence of electronic sub-bandgap trap states is one of the origins of non-radiative recombination pathways [37, 38]. The internal passivation derived from 2D perovskite participation in the final DGPF perovskite film can effectively suppress non-radiative recombination to incur minimal voltage losses. PDS result comes with a characteristic Urbach energy. The Urbach energies, estimated from the PDS spectra are 20.55, 19.7, 19.9, and 23.21 meV for the sample treated with the BABr concentration of 0 mg/ml, 1 mg/ml, 2 mg/ml, and 5 mg/ml, respectively (Supplementary Fig. 14). The lower Urbach energy indicates a lower level of electronic disorder in the perovskite films with a low concentration of BABr treatment, which agrees with the enhancement of V_{OC} [39]. When increasing the BABr concentrations to 5 mg/ml, we observe a gentle band-edge absorption rise, indicating increased energy disorder. As the inherent Urbach energy in 2D perovskite is higher compared to 3D counterparts, this is expected and also consistent with the decreasing device performance when treating with higher concentration of BABr. The PDS result of 2D perovskites is shown in Supplementary Fig. 15, which shows the Urbach energy of 2D perovskite is 38.4 meV.

We further performed electronic structure calculations based on density functional theory (DFT) calculations to investigate the passivation mechanism at BA/perovskite interface. The surface terminated with (110) plane was used for the calculations. Charge density calculations based on the DFT were performed to characterize how amine, including BA molecule, can passivate the $Cs_{0.125}FA_{0.875}Pb(I_{0.85}Br_{0.15})_3$ surfaces. The anti-site defect is modeled, such as Pb_{Br} or Pb_I, known as deep-level defects and the most detrimental defects in perovskite solar cells[40]. As illustrated in Supplementary Fig. 16, the charge distribution is localized around the anti-site defect site, which can produce the recombination center and capture the carriers. After interaction with BA molecule, we first find that the nitrogen (N) will bond with Pb atoms and then the previous anti-site defect can be passivated, shown in Supplementary Fig. 16c, like the perfect surface without defect indicating by

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374 Supplementary Fig. 16b. Without the dopant BA, the localized electron distribution is

375 observed clearly in Supplementary Fig. 16a. The adsorption of BA will make the

376 charge distribution delocalized, indicating that the trap states caused by anti-site

377 defect are passivated. Trap density of states (tDOS) of control and DGPF devices are

378 further examined, showing a much lower tDOS in DGPF devices, which is consistent

379 with DFT calculation (Supplementary Fig. 17).

380 The effectiveness of the DGPF approach has validated in more perovskite

381 systems. In double cation $MA_{0.7}FA_{0.3}PbI_3$ perovskite system, XRD measurement was

382 conducted to analysis the crystal structure of the formed DGPF perovskite film

383 (Supplementary Fig. 18). The perovskite film shows slight peak shift towards higher

384 2θ degrees, which is consistent with the findings from quaternary RbCsMAFA

385 perovskite system. The GIWAXS results in Supplementary Fig. 19 clearly show the

386 2D diffractive peaks for the BABr-treated samples. The formed 2D perovskite top

387 layer consists of layered 2D perovskites with different n values (n=2 & n=3). The

388 device performance based on these narrower-bandgap perovskite ($MA_{0.7}FA_{0.3}PbI_3$,

389 E_g=1.55 eV) are shown in Supplementary Fig. 20. The best-performing

390 $MA_{0.7}FA_{0.3}PbI_3$ PSC with 2 mg/ml BABr post-treatment (E_g=1.56 eV) exhibits a V_{OC}

391 of 1.161 V, a J_{SC} of 22.95 mA/cm^2, and a FF of 77.67%, featuring a high PCE of

392 20.67%. For comparison, the control pure 3D device has a lower PCE of 18.59%. The

393 significantly enhanced V_{OC} for the DGPF PSCs is associated with a significantly

394 reduced V_{OC} deficit, i.e., W_{OC} of 0.40V.

395 This method was also tested in wide-bandgap (WBG) mixed-cation Pb PSCs,

396 which has the significance of being potentially an ideal WBG subcell for tandem

397 perovskite PSCs towards higher efficiency[41, 42]. By means of DGPF approach, the

398 best-performing wide-bandgap $FA_{0.8}Cs_{0.2}Pb(I_{0.7}Br_{0.3})_3$ PSC (E_g=1.73 eV) has a PCE of

399 18.09% with a W_{OC} of 0.48 V and an outstanding V_{OC} of 1.26 V (Supplementary Fig.

400 21) [43]. This is again one of the highest V_{OC}, and lowest W_{OC} in ~1.73 eV bandgap

401 PSCs, to our knowledge [44]. Hysteresis analysis of representative PSCs based on

402 various optical bandgaps is shown in Supplementary Fig. 22 and summarized in

403 Supplementary Table 4. Devices after incorporating BABr exhibit lower *J-V*

hysteresis compared to the control pure 3D PSC device, which is consistent with the scenario that larger BA moieties mitigate or even prohibit ion migration and reduce defect mentioned above. The data of voltage loss analysis in perovskite devices with different bandgaps were summarized in Table 1.

We further proved the effectiveness of DGPF approach in a ~1.53 eV perovskite system ($Cs_{0.03}(FA_{0.97}MA_{0.03})_{0.97}Pb(I_{0.97}Br_{0.03})_3$) with a modified SnO_2 QDs ETL. A champion PCE up to 23.78% (average PCE: 23.24 ± 0.33%, certified PCE: 23.09%, Figure S27) with a maximum V_{OC} of 1.210 V (W_{OC} as low as 0.326 V) was achieved, as shown in Fig. 3d. The bandgap of perovskite was calculated through the combination of EQE and UV-vis absorption spectra (see Supplementary Fig. 23, 24). More details can be found in Supplementary Fig. 25-27 and Supplementary Table 7. To evaluate the $\Delta V_{OC,nr}$, we measured the EQE_{EL} for a complete PSC device operating as a LED in forward voltage bias, as shown in Fig. 3f. The DGPF device exhibited an EQE_{EL} up to 5.78% at an injection current equal to J_{SC} (24.57 mA/cm^2), corresponding to a $\Delta V_{OC,nr}$ of 74 mV, which agreed well with the estimated value from W_{OC}. To the best of our knowledge, 0.326 V W_{OC} is among the lowest in all reported perovskite systems.

In addition to device performance, the operational stability of PSCs is also vital for PSC technology. We first investigated the long-term stability of control and DGPF PSCs (non-encapsulated) under dark storage in the ambient conditions with 30% relative humidity (RH) (Supplementary Fig. 28). The DGPF PSCs showed significantly enhanced resistivity to humidity, virtually no PCE degradation after 45 days. This is attributed to the improved hydrophobicity of perovskite structure after introducing large organic cation (BA). We further studied the stability of encapsulated device under continues simulated sunlight illumination (~35 °C) at open-circuit condition. The DGPF PSCs showed much slower performance degradation compared to pure 3D PSCs. The encapsulated DGPF PSCs retained 62% of the initial PCE after 800 h illumination, while the control 3D PSCs only retain the 25% of the original PCE under the same conditions (Fig. 4). All the device parameters recorded during the stability test (Supplementary Fig. 29a and b), are shown in Supplementary Table 5 and

6. 'Burn-in' exponential degradation regime was clearly observed in both types of devices, which is a common phenomenon for PSCs and organic solar cells [25, 45, 46]. More specifically, both types of PSCs experienced a faster performance degradation process (around 100 h), followed by a slower steady degradation. For the encapsulated DGPF PSCs, the T_{80} (i.e. lose 20% initial PCE) post burn-in lifetime is 700 h under 0.8-sun illumination. However, the T_{80} post burn-in lifetime for pure 3D PSC devices are significantly shorter at ~ 300 h. To exclude the effects of interface layers (particularly the spiro-OMeTAD HTM) and electric load (under maximum power point (MPP) or OC) on the device operational stability, we fabricated perovskite devices with a planar p-i-n structure (Supplementary Fig. 30a and b) and performed long-term stability test of encapsulated devices illuminated under continues 1-sun irradiation by LED lamp at a temperature of ~60 ˚C in air condition as shown in Fig. 4b[45]. At MPP condition, we found that both control and DGPF devices showed obviously decreased degradation rates compared that at OC, which can be ascribed to role of excess charge carrier. Finally, our DGPF devices can retain 91% of initial efficiency after 516 h of continuous illumination operation in ambient air conditions. In comparison, the control device only retained 16% of the original PCE under the same conditions.

In summary, we developed a simple DGPF self-passivation strategy for high performance PSCs, which simultaneously achieved both bulk and interface 2D perovskite passivation of the PSCs. The DGPF strategy dramatically boost the PCE of 1.63 eV quaternary-cation PSCs to 21.54%, with a superb V_{OC} of 1.24 V; we further improved the PCE up to 23.78% (certified 23.09%) with the maximum V_{OC} of 1.21 V in a ~1.53 eV perovskite system, i.e. W_{OC} as low as 0.326 V. Non-radiative recombination losses in perovskite materials and devices can be reduced to as low as 74 mV (from EQE_{EL} measurement), one of the lowest reported to date. The method is universally applicable to PSCs of different bandgaps. Moreover, significantly enhanced operation stability is achieved with the simultaneous 2D perovskite passivation in bulk and interfaces. The DGPF approach paves the way to further approach the theoretical PSC efficiency limit via the elimination of non-radiative

464 recombination decay, and is a step forward to achieve highly efficient PSCs with

465 long-term operational stability.

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Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request

Author contributions

G.L., G.Y. and Y.Y. proposed the idea and designed the experiment. G.Y. and Z.R. fabricated and characterized perovskite solar cells. Z.R., K.L. and Q.L. prepared and characterized the devices for the efficiency certification of PSCs. G.Y. conducted SEM, AFM, XRD, and PL measurements. X.L. and M.Q. carried out GIWAXS measurement and analyzed the results. W.D. and H.W. conducted the EL measurement and discussed the radiative and non-radiative recombination loss analysis. Y.C. performed DFT calculations on the BA molecule passivation under the supervision of T.S. and X.W. B.G. and J.H. helped to measure the Ultrasensitive EQE. D.L. and S.L. contributed to the PLQY measurement. J.L., H.W., and F.Y. carried out the UPS and absorption measurements. H.Y. and S.K.S contributed to the photothermal deflection spectroscopy data. H.Z. contributed to the ToF-SIMS result analysis. Y.Z performed the HRTEM measurement and analyzed the results under the supervision of J.W.. G.L., G.F., Y.Y., G.Y., Z.R., K.L., and X.L. prepared, revised, and finalized the manuscript. All the authors discussed the results and commented on the manuscript.

Competing financial interests

The authors declare no competing financial interests.

Methods

Materials and Methods

Preparation of RbCsMAFA ($Rb_{0.05}Cs_{0.05}[(FA_{0.83}MA_{0.17})]_{0.9}Pb(I_{0.83}Br_{0.17})_3$)

First, a nonstoichiometric precursor solution for $(FA_{0.83}MA_{0.17})Pb(I_{0.83}Br_{0.17})_3$ was prepared by dissolving 1.1 M PbI_2 (TCI), 1 M FAI (Dyesol), 0.22 M $PbBr_2$, and

0.2 M MABr (Dyesol) in 1 mL of a 4 : 1 (v/v) mixture of anhydrous DMF and DMSO. (Please note the volume changes upon dissolving these salts) 40 µL of 1.5 M CsI (Alfa Aesar) pre-dissolved in 1mL DMSO and 40 µL of 1.5 M RbI (Alfa Aesar) pre-dissolved in 1mL of a 4 : 1 (v/v) mixture of anhydrous DMF and DMSO were then added to the as-prepared $(FA_{0.83}MA_{0.17})Pb(I_{0.83}Br_{0.17})_3$ solution, yielding a quadruple cation perovskite composition of $Rb_{0.05}Cs_{0.05}[(FA_{0.83}MA_{0.17})]_{0.9}Pb(I_{0.83}Br_{0.17})_3$. The quadruple perovskite solution was stirred for 6 at room temperature and then filtrated using a 0.45 µm filter before use. For RbCsMAFA film deposition, 50 µL of the perovskite precursor solution was spin-coated onto the substrates at 1000 and 5000 rpm for 10 and 20 s, respectively. 105 µL chlorobenzene was dropped to the perovskite film at 25 s of the spinning process. The perovskite films were then put on a hot plate at 100 °C for 60 min.

Preparation of $MA_{0.7}FA_{0.3}PbI_3$

The $MA_{0.7}FA_{0.3}PbI_3$ precursor solutions were contained 1.25 M (PbI_2:MAI:FAI=1:0.7:0.3) in a mixed solvent of DMF and DMSO (volume radio: 4:1). 12 mg $Pb(SCN)_2$ (Sigma-Aldrich) was then added into 1mL $MA_{0.7}FA_{0.3}PbI_3$ precursor solutions. For $MA_{0.7}FA_{0.3}PbI_3$ film deposition, 50 µL of the perovskite precursor solution was spin-coated onto the substrates at 1000 and 4000 rpm for 5 and 30 s, respectively. 300 µL chlorobenzene was dropped to the perovskite film at 13-15 s of the spinning process. Then the as-deposited film was annealed at 65 ºC for 2 min and then 100 ºC for 10 min.

Preparation of $FA_{0.8}Cs_{0.2}Pb(I_{0.7}Br_{0.3})_3$

The $FA_{0.8}Cs_{0.2}Pb(I_{0.7}Br_{0.3})_3$ precursor solutions were contained 0.8 M FAI, 0.2 M CsI, 0.55 M PbI_2, 0.45 M $PbBr_2$, and 0.55% M $Pb(SCN)_2$ in a mixed solvent of DMF and DMSO (volume radio: 3:1). For $FA_{0.8}Cs_{0.2}Pb(I_{0.7}Br_{0.3})_3$ film deposition, 50 µL of the perovskite precursor solution was spin-coated onto the substrates at 1000 and 4000 rpm for 5 and 30 s, respectively. 300 µL chlorobenzene was dropped to the perovskite film at 13-15 s of the spinning process. The as-prepared film was annealed at 65 ºC for 2 min and then 100 ºC for 10 min.

Preparation of $Cs_{0.03}(FA_{0.97}MA_{0.03})_{0.97}Pb(I_{0.97}Br_{0.03})_3$

The $Cs_{0.03}(FA_{0.97}MA_{0.03})_{0.97}Pb(I_{0.97}Br_{0.03})_3$ precursor solution was prepared with the mixed powders of FAI: MABr: MACl: $PbBr_2$: PbI_2 (molar ratio: 1.41:0.04:0.4:0.04:1.47) in the mixture of DMF: DMSO (4:1, v:v), blended with 3% volume ratio of CsI (1.5 M) stock solution. For $Cs_{0.03}(FA_{0.97}MA_{0.03})_{0.97}Pb(I_{0.97}Br_{0.03})_3$ film deposition, 50 µL of the perovskite solution was spin-coated onto the SnO_2 coated ITO substrate at 1000 and 6000 rpm for 10 and 30s, respectively. 150 µL chlorobenzene was dropped onto the perovskite film at 15-20 s of high-speed spin-coating process. The as-prepared films were annealed at 120 ºC for 1 h in the ambient atmosphere with ~20% RH.

For Dimensionally Graded Passivation method, 100 µL of BABr-IPA solution (the concentrations ranged from 1 to 5 mg/mL) was spin-coated on the as-prepared

691   perovskite films at 5000 rpm for 30 s. Then the perovskite films were annealed at 100

692   ºC for 10 min.

693   Perovskite solar cells fabrication

694   N-i-p solar cells: The indium tin oxide (ITO)–coated glass was sequentially

695   cleaned using deionized water, acetone, and ethanol. All substrates were further

696   cleaned by UV-ozone for 15 min before deposition of SnO_2 ETL. 30 nm SnO_2 QD

697   ETL was deposited on the cleaned ITO substrate by spin-coating as-prepared colloidal

698   SnO_2 QD solution.[14] Following, the as-deposited SnO_2 QD ETL was annealed on a

699   hot plate at 200 °C for 1 h in air. The mixed-cation perovskite was deposited via a

700   one-step spin-coating procedure as mentioned above. 20 μL spiro-OMeTAD solution

701   containing 72.3 mg spiro-OMeTAD (Lumitech), 28.8 μL tert-butylpyridine (t-BP,

702   Sigma-Aldrich), 17.5 μL bis(trifluoromethanesulfonyl)imide (Li-TFSI, Sigma-Aldrich)

703   solution (520 mg in acetonitrile), and 1 mL chlorobenzene was spin-coated onto the

704   perovskite layer at 3000 rpm for 20 s. Finally, a thickness of 80 nm Au was deposited

705   by thermal evaporation.

706   P-i-n solar cells: The PTAA solution (2 mg/mL in toluene) was spin-coated onto

707   the perovskite layer at 5000 rpm for 30s and annealed at 100 °C for 10 min. 1.63 eV

708   perovskite layer was deposited on PTAA layer with the same method based on

709   one-step approach. Then, 30-nm-thick C_{60} layer (electron transport layer) and

710   12-nm-thick SnO_2 layer (buffer layer) were deposited by thermal evaporation and

711   atomic layer deposition, respectively. Finally, 100-nm-thick Cu was thermal

712   evaporated as top metal electrode.

713

714   Solar cell characterization

715   The current-voltage (*J-V*) characteristics of the devices were measured by using a

716   Keithley 2400 Source Meter under standard AM 1.5 G Simulator (SS-F5, Enli

717   Technology Co. Ltd., Taiwan), and the light intensity was calibrated by a standard

718   SRC-2020 Si reference cell. The *J-V* curves were obtained from the range of 1.3 V to

719   -0.1 V with a scan speed of 100 mV/s from both reverse and forward scan direction.

720   The active area of device is 0.09 cm^2, a mask with an aperture area of 0.0625 cm^2 was

721   used to define device area. The stabilized output of the devices was measured by

722   recording the current output of the illuminated device while holding it at a constant

723   voltage near the maximum power point extracted from the *J-V* curve.

724   Solar cell certification

725   Device certification was conducted by Enli Tech. Optoelectronic Calibration Lab.,

726   a photovoltaic certification laboratory accredited by Taiwan Accreditation Foundation

727   (Accreditation Criteria: ISO/IEC 17025:2005).

728

729   Photo-stability test

730   The devices are kept under a white light-emitting diode (LED) array with 0.8 sun

731   intensities, which was calibrated using a standard silicon solar cell (KG 5). The

732   encapsulated devices were exposed to below 20% relative humidity at ~35 °C.

733

734   External quantum efficiency (EQE)

The EQE measurements of photovoltaic device were carried out from 300 to 850 nm using a QE-R 3011 system (Enli Tech, Taiwan).

X-ray diffraction (XRD) and Grazing-incidence wide-angle X-ray scattering (GIWAXS) characterization

The crystal structure and phase of the materials were characterized using an XRD (Rigaku SmartLab X-ray diffractometer) with Cu Kα radiation under operation conditions of 40 kV and 40 mA (The θ-2θ scan mode from 10° to 70° in a step of 0.01°). The GIWAXS measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.3°. The perovskite films for XRD and GIWAXS characterizations were deposited on on SnO_2-coated ITO substrates.

Scanning electron microscopy (SEM)

The morphologies and microstructures were investigated by using a TESCAN $MAIA_3$ field emission scanning electron microscopy. The perovskite films for SEM measurement were prepared on SnO_2-coated ITO substrates.

Atomic force microscopy (AFM)

Bruker NanoScope 8 atomic force microscope was used to measure height and phase profile of perovskite films in the tapping mode. The perovskite films for AFM measurement were prepared on SnO_2-coated ITO substrates.

Photothermal deflection spectroscopy (PDS)

For PDS measurement, the perovskite film was deposited on quartz substrate and then immersed into Fluorinert FC-72 from 3M Corporation. A monochromatic light beam was modulated at 13 Hz by a mechanical chopper to excite the perovskite films from the quartz side. A laser was at the perpendicular side so that it was deflected periodically. A position detector, connected with a lock-in amplifier, was placed on the other side so that the beam deflection signal was measured.

The time-of-flight secondary-ion mass spectroscopy (ToF-SIMS)

The perovskite films were deposited on the ITO substrates for ToF-SIMS measurement. The ToF-SIMS measurements (Model TOF-SIMS V, ION-TOF GmbH) were conducted with the pulsed primary ions from a Cs^+ (3 keV) liquid-metal ion gun or C_{60} (10 keV) for the sputtering and a Bi^+ pulsed primary ion beam for the analysis (25 keV).

Time-resolved photoluminescence and photoluminescence spectra

Photoluminescence measurements of perovskite film on glass were conducted by using an Edinburgh FLSP920 spectrophotometer installed with the excitation source of 485 nm picosecond pulsed diode laser in the average power of 0.15 mW.

779 Ultraviolet-visible (UV-Vis) absorption spectra

780   The absorption spectra of the perovskite films were measured by an UV-vis
781 spectrophotometer (CARY5000, Varian, Australia) in a wavelength range at 300-850
782 nm at room temperature.

783

784 Ultraviolet photoelectron spectroscopy (UPS)

785   The samples for UPS measurements were made by depositing perovskite films on
786 the ITO conductive substrates. Then the UPS measurement was performed using a
787 XPS/UPS system (Thermo Scientific, Escalab 250Xi).

788

789 Photoluminescence quantum efficiency (PLQE)

790   The PLQE of perovskite films was measured using an integrating sphere
791 (Edinburgh instruments) with a 485-nm excitation laser (~125 mW/cm^2) in open-air
792 conditions.

793

794 External quantum efficiency of the electroluminescence (EQE$_{EL}$)

795   The EQE$_{EL}$ of the solar cells was determined by measuring the emitted photons of
796 devices in all directions through an integrated sphere by using a calibrated
797 spectrometer (QE Pro, Ocean Optics), under a constant current density provided by a
798 Keithley 2400 source measure unit. The devices were left at room temperature in
799 open-air conditions.

800

801 Trap density of states (tDOS)

802   Admittance spectra were measured by using an Agilent E4980A meter with an
803 alternating voltage of 20 mV. The frequency-dependence of the capacitance was
804 recorded from 1 kHz to 2000 kHz with zero bias in the dark.

805

806 Transmission electron microscope characterization (TEM)

807   Transmission electron microscopy (TEM) lift-out samples were prepared via
808 focused ion beam (FIB) polishing in a TESCAN GAIA3 FIB-SEM. A covering layer
809 of 1.5 μm thick platinum was deposited by electron beam. The TEM lamella was
810 extracted by FIB with an ion beam of accelerating voltage of 30 kV and current of 7
811 nA and welded to a TEM copper grid by platinum. After that, the TEM lamella was
812 polished to about 300 nm thick with accelerating voltage of 30 kV and current of 100
813 pA. Finally, it was thinned to electron transparency with accelerating voltage of 5 kV
814 and current of 25 pA and accelerating voltage of 2 kV and current of 20 pA.
815 Accelerating voltage for SEM observation and electron beam deposition was kept at 5
816 kV during the whole process. The TEM lift-out sample was sent into TEM chamber in
817 less than one minute after the sample preparation. TEM observations were carried out
818 by using a JEOL ARM200CF transmission electron microscope equipped with a cold
819 field-emission electron gun and double spherical-aberration correctors (CEOS GmbH)
820 operated at 80 kV.

821

822 Density functional theory (DFT) calculations

823   All the calculations were performed based on the DFT calculations using Vienna ab
824   initio simulation package (VASP) code with the standard frozen-core projector
825   augmented-wave (PAW) method. The generalized gradient approximation (GGA) of
826   Perdew-Burke-Ernzerh (PBE) function is employed for exchange-correlation
827   potential. The cut-off energy for basis functions is 400 eV and the k-point mesh was
828   obtained using the Monkhorst-Pack method with a reasonable grid density. Atoms are
829   fully relaxed until the Hellmann-Feynman forces on them are 0.01 eV/Å and the
830   vacuum layer is 15Å, which is long enough to reach the calculation precision. The
831   effect of van der Waals interactions was considered by using the empirical correction
832   method proposed by Grimme (DFT-D3) with the Becke and Johnson (BJ)-damped.
833   Dipole correction was applied to compensate for the diploe interaction.
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Figure 1 | Device architecture and ToF–SIMS profiling of DGPF devices. a, **b**, A

schematic diagram (a) and cross-sectional TEM images (b) of our fabricated DGPF

film deposited on the SnO_2-coated ITO substrate. **c**, TOF-SIMS depth profiles of

DGPF perovskite films deposited on ITO substrates.

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Figure 2 | Crystallinity and Morphology of perovskite films. a, 2D GIWAXS patterns of control and DGPF perovskite films with various concentrations of BABr solution (BABr concentrations: 0 mg/ml, 1 mg/ml, 2 mg/ml, and 5 mg/ml). **b**, Radial intensity profiles averaged over the entire 2D GIWAXS image. **c**, Intensity profiles along the q_z axis. **d**, Schematic of formed 2D/3D perovskite films via DGPF method, in which a thin 2D perovskite capping layer with mixed-dimensionality was formed on top of 3D perovskite films, and 2D perovskite phase can be further produced between the grain boundaries of the 3D counterparts leading to the formation of mixed 2D/3D perovskite. **e**, Top view SEM and surface AFM images of control and DGPF perovskite films with different BABr concentrations.

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Figure 3 | Photovoltaic performance and optoelectronic properties of perovskite solar cells. a, J-V curves obtained from forward and reverse scan directions for the champion PSC device based on 1.63 eV perovskite composition. **b,** External quantum efficiency, and the electroluminescence (EL) spectra for control and DGPF-based perovskite devices. **c**, Calculated EL quantum efficiency derived from the EL spectra at an injection current density of 22 mA/cm^2 (Here, the measured V_{OC} of control (0-BABr) and DGPF (2-BABr) PSCs are 1.16 V and 1.23 V, respectively). **d**, J-V curves of the champion control and DGPF based devices in a ~1.53 eV perovskite system from forward and reverse scan directions. **d**, EQE spectrum of the DGPF based device with an integrated J_{SC} of 24.25 mA/cm^2. **f**, EQE$_{EL}$ as a function of the injection current density for the control and DGPF based PSCs when operating as LEDs.

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Figure 4 | Operational stability of control and DGPF devices. Device Stability parameters of control and DGPF perovskite devices with encapsulation. Data obtained from current density-voltage scans over time for devices. **a**, N-I-P devices are kept under a white light-emitting diode (LED) array with 0.8 sun intensities under open-circuit (OC) condition (20-30% RH, 35-40 °C). **b**, The stability data were determined from maximum power point tracking of P-I-N devices illuminated at 1-sun irradiation by LED lamp in ambient condition (30-40% RH, 60-65 °C).

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1033   **Table 1.** Photovoltaic parameters and voltage loss analysis of the best-performing

1034   PSCs

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a

CH₃—CH₂—CH₂—CH₂—N⁺(H)(H)(H) Br⁻

BABr

3D perovskite
Substrate

2D perovskite
3D perovskite
Substrate

Before annealing

Mixed dimensional 2D perovskites
Uniformly distributed 2D/3D mixture
Substrate

After annealing

b

Graded 2D

Mixed 2D/3D

SnO₂

ITO

100 nm

c

Figure 1

Figure 2

a

Current density (mA/cm²) vs Voltage (V)

1.63 eV

	Reverse	Forward
V_{OC}	1.240	1.239
FF	0.7765	0.7752
J_{sc}	22.37	22.37
PCE	21.54%	21.49%

b

EQE and emitted photon flux (a.u.) vs Energy (eV)

Normalized electroluminescence flux (a.u.)

1.63 eV

EQE (Control)
EQE (DGPF)
EL (Control)
EL (DGPF)
EL/Φ$_{BB}$ (Control)
EL/Φ$_{BB}$ (DGPF)
black body photo flux

EL

c

EL intensity (mW/nm) vs Wavelength (nm)

External EL quantum efficiency ($Q_{e,EL}$)

1.63 eV

Control
DGPF

$Q_{e,EL}$

$Q_{e,EL}$=0.85%

$Q_{e,EL}$=0.065%

d

Current density (mA/cm²) vs Voltage (V)

1.53 eV

Control Forward
Control Reverse
DGPF Forward
DGPF Reverse

e

EQE (%) vs Wavelength (nm)

Intergrated J_{SC} (mA/cm²)

1.53 eV

DGPF

J_{SC}=24.25 mA/cm²

f

EQE$_{EL}$ (%) vs Current density (mA/cm²)

1.53 eV

Control
DGPF

5.78%

1.23%

Figure 3

a Encapsulated n-i-p devices in air at 35-40 °C under OC

b Encapsulated p-i-n devices in air at 60-65 °C under MPP

Figure 4

Perovskite composition	Conditions	E_g^a (eV)	V_OC (V)	J_SC (mA cm^{-2})	FF (%)	PCE (%)	$\Delta V_\text{OC,SQ}$[b] ($\Delta V_\text{OC,rad}$[c]) (V)	$\Delta V_\text{OC,nr}$[d] (V)
MA$_{0.7}$FA$_{0.3}$PbI$_3$	Control	1.555	1.094	22.68	74.77	18.58	0.273	0.188
	DGPF	1.561	1.160	22.95	77.57	20.67	0.273	0.128
RbCsMAFA	Control	1.628	1.161	22.25	75.92	19.61	0.283	0.184
(I:Br=0.83:0.17)	DGPF	1.632	1.240	22.37	77.65	21.54	0.283	0.109
FA$_{0.8}$Cs$_{0.2}$Pb(I$_{0.7}$Br$_{0.3}$)$_3$	Control	1.733	1.212	18.24	73.21	16.18	0.285	0.236
	DGPF	1.737	1.260	18.44	77.82	18.08	0.285	0.192
Cs$_{0.03}$(FA$_{0.97}$MA$_{0.03}$)$_{0.97}$	Control	1.533	1.154	24.60	76.50	21.71	0.272	0.107
Pb(I$_{0.97}$Br$_{0.03}$)$_3$	DGPF	1.536	1.210	24.57	80.00	23.78	0.272	0.054

Note:

[a]E_g was derived from the average value of E_g^IP and E_g^Tauc.

[b]$\Delta V_\text{OC,SQ}$ was calculated (as a function of bandgap) using detailed balance principle.

[c]$\Delta V_\text{OC,rad}=E_g/q-V_\text{OC,rad}$, and this is only available for 1.63 eV perovskites shown in this table.

[d]$\Delta V_\text{OC,nr}$ was calculated from W_OC and $\Delta V_\text{OC,SQ}$ or $\Delta V_\text{OC,rad}$.