

Two-/Three-Dimensional Perovskite Bilayer Thin Films Post-Treated with Solvent Vapor for High-Performance Perovskite Photovoltaics

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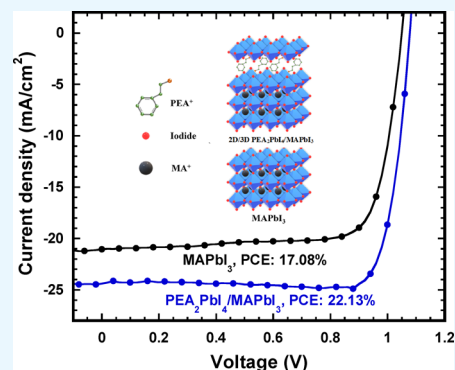
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ABSTRACT: Perovskite photovoltaics (PPVs) using three-dimensional (3D) perovskites incorporated with two-dimensional (2D) perovskites have drawn great concentration in both academic and industrial sectors. Here, we report high performance of PPVs based on the 2D/3D perovskite bilayer thin film post-annealed with solvent vapor. The 2D/3D perovskite bilayer thin film post-annealed with solvent vapor possesses enlarged crystal size and crystallinity and blue-shifted photoluminescence compared to a 3D MAPbI₃ thin film. Moreover, compared to the PPVs based on a 3D perovskite thin film, enlarged built-in potential, suppressed charge carrier recombination, boosted charge transport, and reduced charge carrier extraction time are observed from the PPVs based on the 2D/3D perovskite bilayer thin film post-annealed with solvent vapor. As a result, perovskite solar cells exhibit a power conversion efficiency of 22.13% and dramatically enhanced stability, and perovskite photodetectors show a photoresponsivity of 1.38 AW⁻¹, detectivity of 6.52 × 10¹⁴ cm Hz^{1/2} W⁻¹, and linear dynamic range of over 167 dB at room temperature. These results demonstrate that we develop a simple method to approach high-performance PPVs by the 2D/3D perovskite bilayer thin film.

KEYWORDS: perovskite photovoltaics, 2D/3D perovskite bilayer thin film, power conversion efficiency, photodetectivity, stability



1. INTRODUCTION

Three-dimensional (3D) hybrid inorganic–organic perovskites have been mightily studied for approaching high-performance perovskite photovoltaics (PPVs) including perovskite solar cells (PSCs) and perovskite photodetectors (PPDs).^{1–8} Efficient PSCs and ultrasensitive PPDs by 3D perovskites have been demonstrated.^{1–8} However, 3D perovskites were intrinsically sensitive to moisture and oxygen, which retarded the long-term stability of PPVs.^{9–11} Through partial substitution of hydrophilic ammonium with organic hydrophobic groups to create two-dimensional (2D) perovskites over 3D perovskites, stable PPVs have been reported.^{3,12–20} The 2D/3D perovskite bilayer thin films, utilizing both optoelectronic properties of 3D perovskites and waterproof functionalities of 2D perovskites, were a facile way to approach high-performance PPVs.^{13,21–23}

In the past years, many attempts have been dedicated to developing high-performance PPVs using 2D/3D perovskite bilayer thin films.^{3,12–20} Smith et al. reported stable 2D perovskites, where methylammonium (MA⁺) was partially substituted by hydrophobic phenethylammonium (PEA⁺).¹² Tsai et al. reported over 12% power conversion efficiency (PCE) from the PSCs by the butylammonium-based perovskites.¹⁸ Recently, Shi et al. reported stable and efficient (a PCE of 17.3%) PSCs using the quasi-2D (4FPEA)₂(MA)₄PbI₆ thin film (where 4FPEA is 4-fluoro-

phenethylammonium).³ However, large alkyl groups within ammonium cations that are used to create 2D perovskites are typical insulating molecules, which inhibit charge transport, resulting in a lower short-circuit photocurrent (J_{SC}) compared to those by 3D perovskite thin films.^{13,24–26} Various approaches have been attempted to address the poor charge transport of 2D perovskites.^{27–29} Typically, hydrophobic organic spacers, for example, PEA⁺ and 4FPEA⁺, were dissolved into *N,N*-dimethylformamide (dimethyl sulfoxide or their mixtures) to make the 2D/3D perovskite bilayer thin films.^{3,30} Park et al. reported boosted PCEs from the PSCs by the 2D/3D perovskite bilayer thin films treated with alcohol solvents.²⁸ Loo's group has elucidated the role of Lewis basicity of the processing solvents and reported that the solvent with a high Gutmann donor number (D_N) could coordinate with Pb²⁺ strongly, which could inhibit iodide coordination, resulting in boosted device performance.³¹

Here, high-performance PPVs (both PSCs and PPDs) based on the PEA₂PbI₄/MAPbI₃ bilayer thin film post-annealed with

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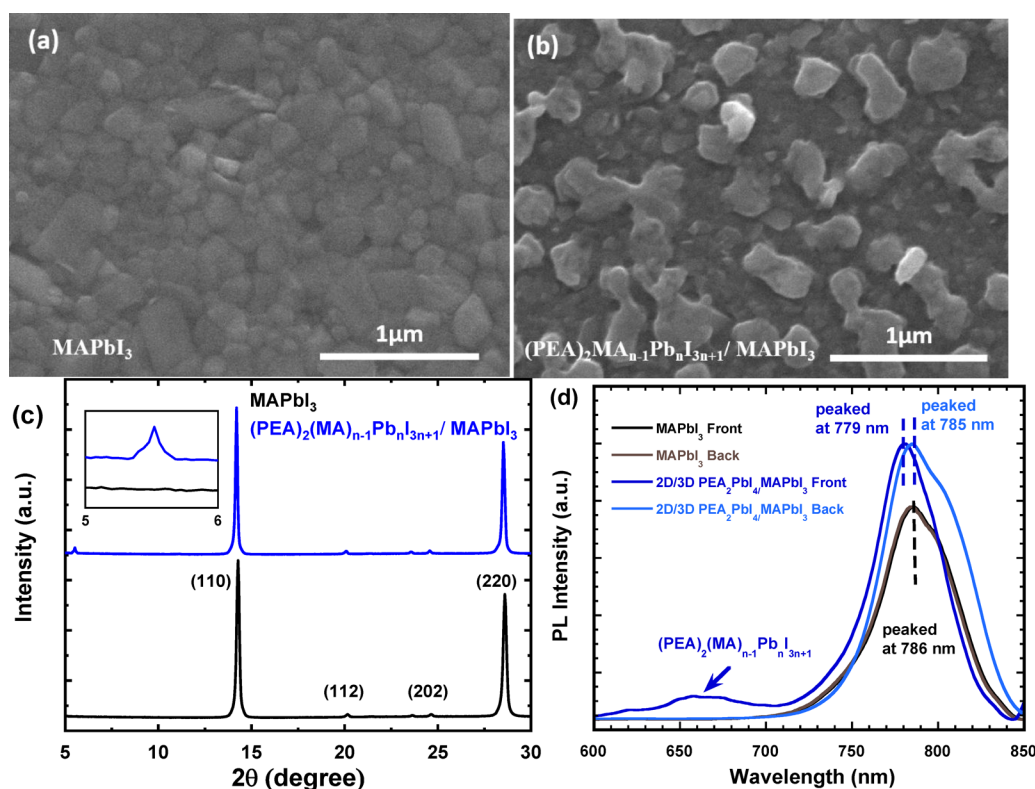


Figure 1. Top view SEM images of (a) the 3D MAPbI₃ thin film and (b) PEA₂PbI₄/MAPbI₃ bilayer thin film; (c) XRD patterns for the 3D MAPbI₃ thin film and PEA₂PbI₄/MAPbI₃ bilayer thin film (the insert is the enlarged diffraction of XRD patterns at a low degree); and (d) photoluminescence (PL) spectra of the 3D MAPbI₃ thin film and PEA₂PbI₄/MAPbI₃ bilayer thin film illuminated from both the front and back sides.

1-butanol vapor are reported. Compared to the 3D MAPbI₃ thin film, the PEA₂PbI₄/MAPbI₃ bilayer thin film post-annealed with 1-butanol vapor possesses enlarged crystal size, superior crystallinity, and blue-shifted photoluminescence (PL). Moreover, the PPVs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film post-annealed with 1-butanol vapor exhibit enlarged built-in potential, suppressed charge carrier recombination, boosted charge transport, and reduced charge carrier extraction time, as compared with those based on the 3D MAPbI₃ thin film. Thus, compared to the PPVs based on the 3D MAPbI₃ thin film, the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film post-annealed with vapor exhibit a PCE of 22.13% and dramatically enhanced stability. Moreover, at room temperature (RT), the PPDs of the PEA₂PbI₄/MAPbI₃ bilayer thin film post-annealed with vapor show a significantly reduced dark current density, photoresponsivity of 1.38 AW⁻¹, detectivity of 6.52 × 10¹⁴ Jones (1 Jones = 1 cm Hz^{1/2} W⁻¹), and linear dynamic range of over 167 dB.

2. RESULTS AND DISCUSSION

The scanning electron microscopy (SEM) images of the 3D MAPbI₃ thin film and the PEA₂PbI₄/MAPbI₃ bilayer thin film post-annealed by 1-butanol vapor are shown in Figure 1a,b. 1-Butanol solvent is used to post-treat the PEA₂PbI₄/MAPbI₃ bilayer thin film because it possesses a large *D_N*, which could inhibit the iodide coordination, resulting in a boosted device performance.³¹ Compared to the 3D MAPbI₃ thin film, the PEA₂PbI₄/MAPbI₃ bilayer thin film post-annealed with 1-butanol vapor possesses a large amount of discretely distributed secondary 2D PEA₂PbI₄ crystals over the 3D MAPbI₃ thin film. The 3D MAPbI₃ thin film possesses a crystal

size of ~100 nm, whereas the PEA₂PbI₄/MAPbI₃ bilayer thin film possesses a crystal size of ~400 nm, thus boosted charge transport; consequently, the PPVs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film is expected to exhibit enlarged enhanced *J_{SC}*.

Figure 1c presents the X-ray diffraction (XRD) patterns of the 3D MAPbI₃ thin film and PEA₂PbI₄/MAPbI₃ bilayer thin film. Both thin films possess strong peaks at 2θ of 14.3, 20.2, 24.7, and 28.6°, which are ascribed to the (110), (112), (202), and (220) planes, respectively.^{32–34} The full width at half maximum (FWHM) value at the (110) plane observed from the 3D MAPbI₃ thin film is 0.17°, whereas the FWHM value at the (110) plane observed from the PEA₂PbI₄/MAPbI₃ bilayer thin film is 0.11°. These low FWHM values indicate that both thin films possess large crystallinity, which is ascribed to the one-step self-assembled method used for the preparation of the 3D MAPbI₃ thin film.³¹ A weak peak at 2θ of 5.5° (the insert of Figure 1c) observed from the PEA₂PbI₄/MAPbI₃ bilayer thin films indicates that the 2D PEA₂PbI₄ is created above the 3D MAPbI₃ thin film.⁴

The PL spectra of the 3D MAPbI₃ thin film and PEA₂PbI₄/MAPbI₃ bilayer thin film are displayed in Figure 1d. Two different thin films possess a similar absorption spectrum, but the PEA₂PbI₄/MAPbI₃ bilayer thin film exhibits a slightly blue-shifted PL spectrum, which originated from the existence of a high *n*-value 2D perovskite component (Figure S1, SI).³ Furthermore, the 3D MAPbI₃ thin film exhibits an identical PL spectrum illuminated either from the front side or the backside. While the PL spectrum of the PEA₂PbI₄/MAPbI₃ bilayer thin film illuminated from the front side is different from that illuminated from the backside. Such a difference in PL spectra

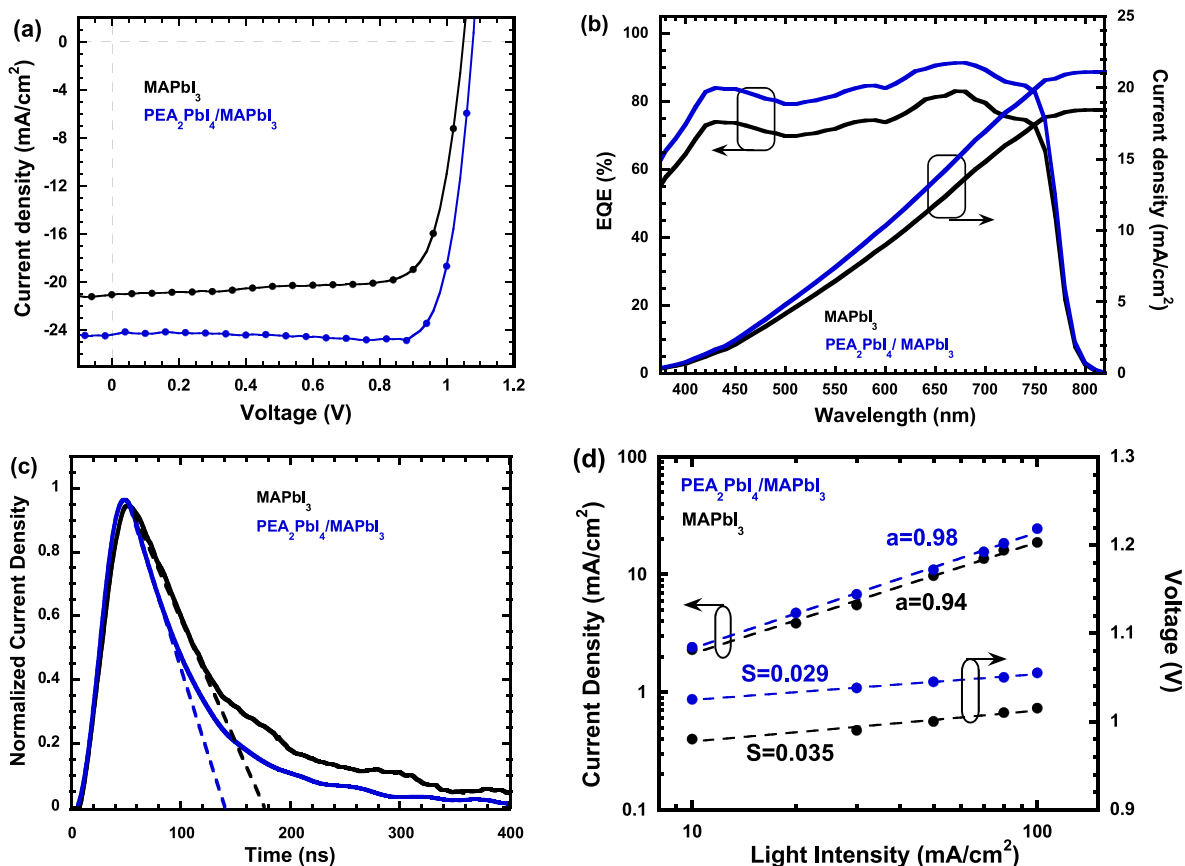


Figure 2. (a) J - V characteristics of PSCs, (b) EQE spectra and integrated J_{SC} of PSCs, (c) normalized transient photocurrent curves of PSCs, and (d) light intensity dependence of J_{SC} and V_{OC} for PSCs, where the PSCs are fabricated using either the 3D MAPbI₃ thin film or PEA₂PbI₄/MAPbI₃ bilayer thin film.

further confirms that the 2D PEA₂PbI₄ thin layer is formed above the 3D MAPbI₃ thin film.^{3,4,12–17} In addition, a broad peak located at ~660 nm within the PEA₂PbI₄/MAPbI₃ bilayer thin film further demonstrates the high n value of the 2D perovskite structure.³ These results indicate the disparate phase distribution for the PEA₂PbI₄/MAPbI₃ bilayer thin film.

The photovoltaic properties of the PEA₂PbI₄/MAPbI₃ bilayer thin film are studied through the investigation of the PPVs with a device architecture of ITO/PTAA/perovskite active layer/C₆₀/BCP/Al, where ITO is indium tin oxides and acts as the anode, PTAA is poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] and serves as the hole extraction layer, the perovskite active layer is either the PEA₂PbI₄/MAPbI₃ bilayer thin film or 3D MAPbI₃ thin film, C₆₀ is fullerene and acts as the electron extraction layer, BCP is bathocuproine and is used as the hole-blocking layer, and Al is aluminum and acts as the cathode. The current density versus voltage (J - V) characteristics of the PSCs by the 3D MAPbI₃ thin film and PSCs by the PEA₂PbI₄/MAPbI₃ bilayer thin films are shown in Figure 2a (and Figure S2). Table S1 summarizes the device performance parameters of PSCs. At a scan rate of 0.60 V s⁻¹, the PSCs based on the 3D MAPbI₃ thin film exhibit a V_{OC} of 1.04 V, J_{SC} of 21.05 mA cm⁻², and fill factor (FF) of 78%, with a PCE of 17.08%. These device performance parameters are consistent with the reported values from the PSCs with a similar device structure.^{35–38} The best device performance of the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film exhibit a V_{OC} of 1.08 V, J_{SC} of 24.39 mA cm⁻², and FF of 84%, with a PCE of 22.13%, which is an

approximately 30% enhancement compared to that based on the 3D MAPbI₃ thin film.

The external quantum efficiency (EQE) spectra and integrated J_{SC} of PSCs are shown in Figure 2b. Compared to the PSCs based on the 3D MAPbI₃ thin film, the EQE spectrum of the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film exhibits a distinct enhancement from 375 to 760 nm. By integration of the EQE spectrum, the integrated J_{SC} values are estimated. An integrated J_{SC} of 19.94 mA cm⁻² is for the PSCs based on the 3D MAPbI₃ thin film, and an integrated J_{SC} of 22.53 mA cm⁻² is for the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film. Both the integrated and extracted (the J - V characteristics Figure 2a) J_{SC} values are nearly the same.

The transient photocurrent (TPC) measurement is used to estimate the charge carrier extraction time of PSCs for investigating the underlying physics of enhanced J_{SC} from the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film.^{34–42} Figure 2c displays the normalized TPC curves of PSCs. The charge carrier extraction time for the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film is estimated to be 141 ns, which is shorter than that (177 ns) for the PSCs based on the 3D MAPbI₃ thin film, revealing that the charge carrier extraction is efficient and the charge carrier recombination is suppressed within the PSCs. Thus, the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film exhibit enhanced J_{SC} . Moreover, the extracted charge carrier densities of the PSCs based the 3D MAPbI₃ thin film are smaller than those based on the PEA₂PbI₄/MAPbI₃ bilayer thin film (Figure S3), which

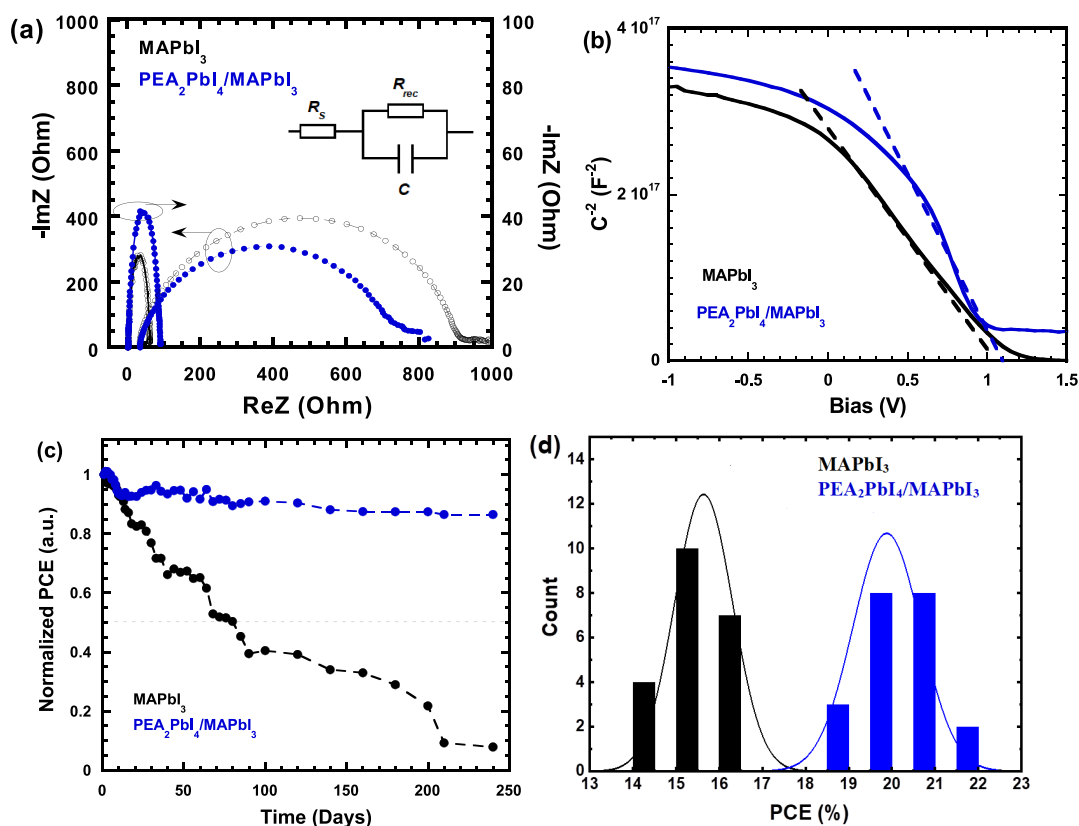


Figure 3. (a) Nyquist plots of PSCs measured in the dark and at an applied voltage close to V_{OC} and (b) Mott–Schottky analysis for the trap density and built-in potential of PSCs. (c) Normalized shelf stability and (d) histograms of PCEs of PSCs, where the PSCs are fabricated using either the 3D MAPbI₃ thin film or PEA₂PbI₄/MAPbI₃ bilayer thin film.

further indicates that the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film exhibit boosted J_{SC} .

Figure 2d presents the light intensity dependence of J_{SC} and V_{OC} of PSCs. Both the J_{SC} and V_{OC} of PSCs depend on light intensity (I). According to the power law of $J_{SC} \propto I^\alpha$ (where α is the scaling exponent),⁴³ an α of 0.94 is observed from the PSCs based on the 3D MAPbI₃ thin film, whereas an α of 0.98 is observed from the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film. As the α value is close to 1, the nongenerate charge carrier recombination is suppressed.⁴³ Thus, the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film exhibit enhanced J_{SC} and consequently boosted PCEs. Moreover, based on $V_{OC} \propto S \ln(I)$ (where S is the slope),⁴³ an S of 0.035 is observed from the PSCs based on the 3D MAPbI₃ thin film, whereas an S of 0.029 is observed from the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film. As S approaches $\frac{kT}{q}$ (0.026) (where k is the Boltzmann constant, T is the absolute temperature, and q is the elementary charge), the trap-assisted charge carrier recombination within the PSCs is suppressed. Thus, a high α and small S observed from the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film indicate that the charge carrier recombination is suppressed, resulting in enhanced J_{SC} and consequently boosted PCE.

Figure 3a displays the Nyquist plots of PSCs measured in the dark and under an applied voltage at $\sim V_{OC}$. As the IS is conducted in the dark and under an applied voltage at V_{OC} , the charge carrier recombination resistance (R_{rec}) is minimized and the charge transfer resistance (R_{CT}) is dominated in PSCs.^{43,44} Thus, a simplified equivalent circuit is presented in the inset of Figure 3a, where R_s , the sheet resistance of the conductive

electrode, is the same, which is based on the identical device structure of PSCs under the investigation.^{43,44} The R_{CT} is affected by the perovskite photoactive layers. The semicircle presented in Figure 3a indicates that not only the RC circuit model is accurate (insert of Figure 3a) but also the transport pathways are homogeneous without discernible multiple interfacial boundaries.⁴⁵ Hence, R_{CT} values for the PSCs based on the 3D MAPbI₃ thin film and the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film are 1002 and 803 Ω , respectively. A smaller R_{CT} observed from the PSCs by the PEA₂PbI₄/MAPbI₃ bilayer thin film is ascribed to superior surface coverage, optimal film morphology, and suppressed defect-induced traps. Thus, reduced R_{CT} indicates that charge transport is boosted, resulting in enhanced J_{SC} and PCEs for the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film.

The impedance spectra (IS) (Nyquist plots) of PSCs measured under white illumination with a light intensity of 100 mW cm⁻² and at an applied voltage of $\sim V_{OC}$ are shown in Figure 3a. Under these conditions, the charge carrier recombination resistance (R_{rec}) is dominated within PSCs. R_{rec} values of 60 and 90 Ω are observed from the PSCs based on the 3D MAPbI₃ thin film and the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film, respectively. A larger R_{rec} indicates that the PSCs possess a suppressed charge carrier recombination. Therefore, boosted J_{SC} is observed from the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film.

The charge carrier mobilities of the 3D MAPbI₃ thin film and PEA₂PbI₄/MAPbI₃ bilayer thin film are further investigated through the space charge limited current method based on the Mott–Gurney law,^{46,47} and the results are shown in

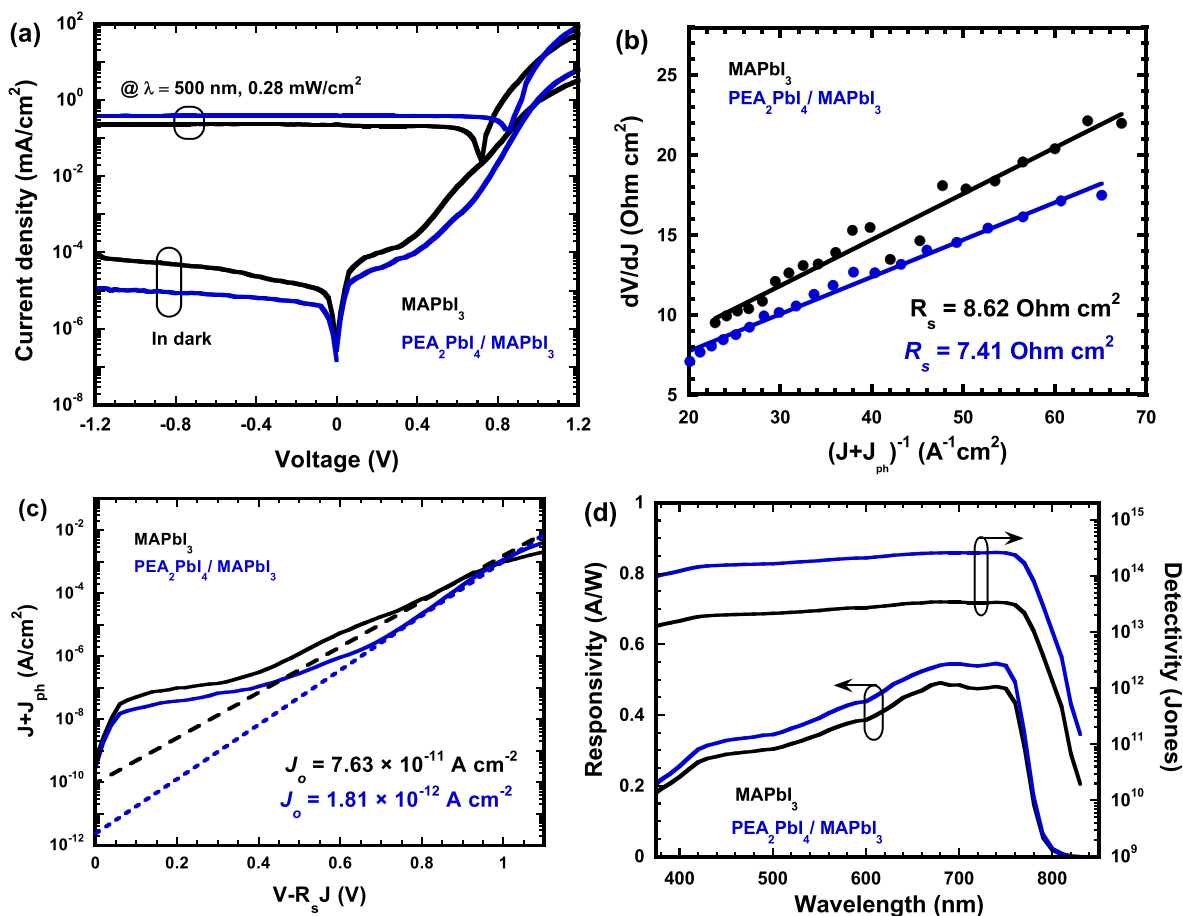


Figure 4. (a) J – V characteristics of PPDs measured both in the dark and under monochromatic illumination at a wavelength of 500 with a light intensity of 0.28 mW/cm^2 at room temperature for PPDs, (b) plot of $\frac{dV}{dJ}$ versus $(J_{ph} + J)^{-1}$ and linear fitting of PPDs, (c) plot of $(J_{ph} + J)^{-1}$ versus $(V - R_s J)$ and the linear fitting of PPDs, (d) responsivity and detectivity versus wavelength for PPDs measured at a bias of -0.10 V , where the PPDs are fabricated using either the 3D MAPbI_3 thin film or $\text{PEA}_2\text{PbI}_4/\text{MAPbI}_3$ bilayer thin film.

Figures S4 and S5 (Scheme S3). A hole mobility of $6.62 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and electron mobility of $5.94 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are observed from the 3D MAPbI_3 thin film. A hole mobility of $7.91 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and electron mobility of $7.16 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ are observed from the $\text{PEA}_2\text{PbI}_4/\text{MAPbI}_3$ bilayer thin film. Thus, the $\text{PEA}_2\text{PbI}_4/\text{MAPbI}_3$ bilayer thin film exhibits both enhanced hole and electron mobilities, indicating that the charge transport is boosted. As a result, enhanced J_{SC} and enlarged FF are observed from the PSCs based on the $\text{PEA}_2\text{PbI}_4/\text{MAPbI}_3$ bilayer thin film.

To understand an enlarged V_{OC} from the PSCs based on the $\text{PEA}_2\text{PbI}_4/\text{MAPbI}_3$ bilayer thin film, the J – V characteristics of PSCs are measured in the dark and the results are shown in

Figure 4a. V_{oc} is described as $V_{oc} = \frac{nkT}{q} \ln\left(\frac{J_{sc}}{J_d}\right)$,^{40–42} where n is the ideality factor (approaches 2) for PSCs,⁴⁶ k is the Boltzmann constant, T is the absolute temperature, q is the electron charge, and J_d is the reverse dark current density. It is concluded that the suppressed dark current density is a response for the enlarged V_{OC} . It is found that PSCs based on the $\text{PEA}_2\text{PbI}_4/\text{MAPbI}_3$ bilayer thin film exhibit lower dark current densities than those based on the 3D MAPbI_3 thin film. Thus, the PSCs based on the $\text{PEA}_2\text{PbI}_4/\text{MAPbI}_3$ bilayer thin film possesses larger V_{OC} with respect to that based on the 3D MAPbI_3 thin film.

Both the built-in potential (V_{bi}) and interfacial charge density (N) of PSCs are estimated based on the capacitance versus voltage (C – V) characteristics of PSCs. According to the Mott–Schottky law of $C^{-2} = \frac{2(V_{bi} - V)}{qe\epsilon_0 A^2 n_c}$ (where V is the applied bias, q is the elementary charge, ϵ is the dielectric constant of perovskites, ϵ_0 is the vacuum permittivity, n_c is the charge carrier density, and A is the active area.), the V_{bi} is the intercept on the bias of the linear fitting line and the N is obtained from the slope of the linear fitting.^{35,48} The C^{-2} – V plot of PSCs is shown in Figure 3b. The PSCs based on the $\text{PEA}_2\text{PbI}_4/\text{MAPbI}_3$ bilayer thin film exhibit a V_{bi} of 1.10 V, which is larger than that (1.04 V) based on the 3D MAPbI_3 thin film. These results indicate that the PSCs based on the $\text{PEA}_2\text{PbI}_4/\text{MAPbI}_3$ bilayer thin film exhibit larger V_{OC} compared to that based on the 3D MAPbI_3 thin film. Moreover, the slope of the C^{-2} – V line for the PSCs based on the 3D MAPbI_3 thin film is estimated to be -2.69×10^{17} , which is higher than -3.95×10^{17} based on the $\text{PEA}_2\text{PbI}_4/\text{MAPbI}_3$ bilayer thin film. Such a larger absolute slope value observed from the PSCs based on the $\text{PEA}_2\text{PbI}_4/\text{MAPbI}_3$ bilayer thin film indicates that PSCs possess a smaller interfacial charge density.^{49,50} As a result, the surface charge carrier recombination is suppressed, which results in enhanced J_{SC} for the PSCs based on the $\text{PEA}_2\text{PbI}_4/\text{MAPbI}_3$ bilayer thin film.

The shelf stability of unencapsulated PSCs is tested in ambient conditions. As indicated in Figure 3c, the PSCs based on the 3D MAPbI₃ thin film drop their PCEs to 45% after 85 days. Under the same condition, the PCE values of the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film maintain 86.5% of their initial PCEs for 240 days. Both PSCs show degradation in J_{SC} after 240 days (Figure S6), but the PSCs based on the 3D MAPbI₃ thin film decreased from 1.04 to 0.98 V after 240 days, whereas the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film shows negligible degradation in V_{OC} after 240 days. Furthermore, the PSCs based on the 3D MAPbI₃ thin film present a significantly declined FF, whereas the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film maintain nearly the same level of the FF for 240 days. Thus, compared to PSCs based on the 3D MAPbI₃ thin film, the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film possess dramatically enhanced stability, which reveals that the 2D perovskite layer plays a very important role in manufacturing long-term stable PSCs and preventing the 3D perovskite layer underneath from moisture.

The reproducibility of PSCs is further investigated. The statistical histograms of PCEs with Gaussian fitting for PSCs from over 20 devices are shown in Figure 3d and Figure S7. The PSCs based on either the 3D MAPbI₃ thin film or 2D/3D PEA₂PbI₄/MAPbI₃ bilayer thin film display a compact distribution of device performance parameters, which indicates good reproducibility of PSCs. With respect to that based on the 3D MAPbI₃ thin film, the PSCs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film present a narrower distribution, indicating that the PSCs possess superior reproducibility. Such high reproducibility is ascribed to the uniform and homogeneous film morphology of the PEA₂PbI₄/MAPbI₃ bilayer thin film.^{51,52}

PPDs are also investigated. The J - V characteristics of PPDs measured both in the dark and under monochromatic illumination at a λ of 500 nm with a light intensity of 0.28 mW/cm² at room temperature (RT) are shown in Figure 4a. At a bias of -0.10 V, the dark current density (J_d) observed from the PPDs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film is 4.20×10^{-9} A cm⁻², which is almost three times lower than that (1.14×10^{-8} A cm⁻²) based on the 3D MAPbI₃ thin film. The decreased J_d indicates that the leakage current from the PPDs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film is suppressed. The low dark current density is attributed to the reduced defects within the PEA₂PbI₄/MAPbI₃ bilayer thin film (Figure 3b) and indicates that the PPDs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film possess boosted projected detectivity (D^*).⁵² Moreover, under monochromatic illumination at $\lambda = 500$ nm with a light intensity of 0.28 mW/cm² at RT, the photocurrent density (J_{ph}) of the PPDs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film is 3.85×10^{-4} A cm⁻², which is higher than that (2.26×10^{-4} A cm⁻²) based on the 3D MAPbI₃ thin film. The responsivity (R) is described as $R = \frac{J_{ph}}{L_{light}}$ (where L_{light} is the incident light intensity).⁵² An R of 0.81 A W⁻¹ is observed from the PPDs based on the 3D MAPbI₃ thin film, whereas an R of 1.38 A W⁻¹ is observed from the PPDs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film.

Based on the J - V curves of PPDs measured in the dark, the J - V curves are extracted to estimate the saturated dark current densities (J_0).^{7,52} J_0 , a key factor determining the D^* of photodetectors (PDs), is related to the charge carrier

recombination and band-to-band thermal emission in PDs.⁵³⁻⁵⁵ Due to the complicated and expensive setup, J_0 is relatively difficult to be measured,^{7,52} but J_0 can be estimated

since J_0 is described as $J = J_0 \left[\exp \left(\frac{q(V - JR_s)}{nk_b T} \right) - 1 \right] - J_{ph}$

(where J is the total current density, q is the elementary electron charge, V is the applied voltage, R_s is the series resistance, n is the idea factor, k_b is the Boltzmann constant, and T is the absolute temperature).⁵³⁻⁵⁵ Figure 4b displays the plot of $\frac{V}{J}$ versus $(J_{ph} + J)^{-1}$ and linear fitting of PPDs. The R_s

value is extracted from the linear fitting intercept (see detailed calculation in the SI). R_s values of 8.62 and 7.41 Ω are calculated for the PPDs based on the 3D MAPbI₃ thin film and PEA₂PbI₄/MAPbI₃ bilayer thin film, respectively. A smaller R_s observed from the PPDs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film indicates that PPDs possess a higher J_{ph} compared to that based on the 3D MAPbI₃ thin film. Figure 4c exhibits the $\ln(J + J_{ph})$ versus $(V - R_s J)$ characteristics and linear fitting intercepts of PPDs. A J_0 of 1.18×10^{-12} A cm⁻² is estimated for the PPDs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film, whereas a J_0 of 7.63×10^{-11} A cm⁻² is estimated for the PPDs based on the 3D MAPbI₃ thin film. Thus, compared to the PPDs based on the 3D MAPbI₃ thin film, a higher J_{ph} and a lower J_0 were observed from the PPDs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film further, which indicates that PPDs exhibit both higher R and D^* .

The D^* is described as $D^* = \frac{R}{\sqrt{2qJ_d}} = \frac{J_{ph}/L_{light}}{\sqrt{2qJ_d}}$,⁵⁶ (where L_{light}

is the light intensity, J_d is the dark current density, and q is the elementary electron charge.). At a λ of 500 nm with a light intensity of 0.28 mW cm⁻² and under an external bias of -0.10 V, a D^* of 5.66×10^{13} Jones (1 Jones = 1 cm Hz^{1/2} W⁻¹) is observed from the PPDs based on the 3D MAPbI₃ thin film, whereas a D^* of 6.52×10^{14} Jones is observed from the PPDs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film. Note that the above D^* is solely calculated based on the measured dark current, probably resulting in a higher D^* with respect to the real detectivity, since both the thermal (Johnson) noise and flicker noise $1/f$ (where f is the frequency) are neglected.⁵⁶⁻⁵⁸ Nevertheless, D^* is acceptable because the noise current is in the same magnitude as the shot noise originating from the dark current and is generally frequency-independent for PDs with a vertical photodiode device structure.^{57,59,60}

Based on the EQE spectra, both R and D^* over spectral response are calculated according to $R = EQE \times \frac{q}{hv} = EQE \times \frac{\lambda}{1240}$ and $D^* = \frac{R}{\sqrt{2qJ_d}}$. Figure 4d presents R and D^* versus wavelength from 375 to 830 nm. At RT, the PPDs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film exhibit significantly higher R and D^* compared to those from the PPDs based on the 3D MAPbI₃ thin film. For example, the PPDs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film exhibit over 10^{14} Jones D^* , which is 10 times higher than those based on the 3D MAPbI₃ thin film. Moreover, this value is higher than that of Si-based PDs in the spectral range from 375 to 700 nm.⁷ Such high detectivity at RT is synergistically derived from high J_{ph} and very low J_d .^{54,55,61}

The linear dynamic range (LDR) described as the photocurrent correlated with a linear response along with the incident light intensity is further investigated. The LDR is described by $LDR = 20 \log (J_{ph}/J_d)$, where J_{ph} is the photocurrent measured at a light intensity of 1 mW/cm² and

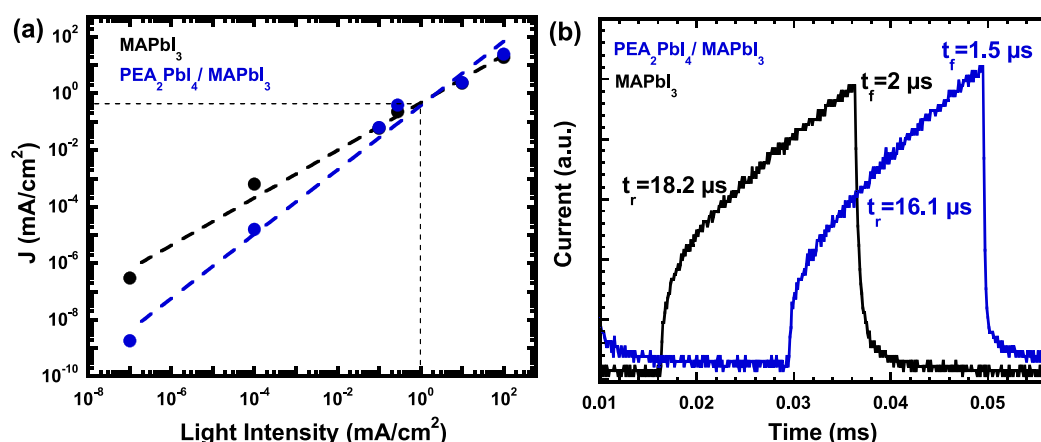


Figure 5. (a) Linear dynamic range (LDR) of PPDs, (b) temporal photocurrent response of PPDs measured with an optical chopper (a frequency of 2 kHz) controlled at a wavelength of 532 nm laser pulse, where the PPDs are fabricated using either the 3D MAPbI₃ thin film or PEA₂PbI₄/MAPbI₃ bilayer thin film.

J_d is the dark current.^{52,54} Figure 5a displays the J_{ph} versus the light intensities for PPDs at RT. An LDR of ~ 122 dB observed from the PPDs based on the 3D MAPbI₃ thin film is smaller than that (~ 167 dB) observed from the PPDs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film. Both are higher than those from Si-based PDs (120 dB, at 77 K) and InGaAs-based PDs (66 dB, at 4.2 K).⁵⁴

The temporal photocurrent response time of PPDs is another important device parameter of PDs.⁶² The response time of PDs is significantly related to the charge transport and collection. The rise and fall times are defined as the time interval required for the photoresponse to rise/decay from 10/90 to 90/10% of its peak photocurrent value, respectively.⁶² The temporal photocurrent responses of PPDs measured with an optical chopper (a frequency of 2 kHz) controlled by a 532 nm λ laser pulse are shown in Figure 5b. A rise time of 18.2 μs and a fall time of 2.0 μs are observed from the PPDs based on the 3D MAPbI₃ thin film, whereas a rise time of 16.1 μs and a fall time of 1.5 μs are observed from the PPDs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film. The faster response times observed from the PPDs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film are attributed to the enhanced charge carrier transport and suppressed defects of the PEA₂PbI₄/MAPbI₃ bilayer thin film.

3. CONCLUSIONS

In summary, we reported the formation of the PEA₂PbI₄/MAPbI₃ bilayer thin films post-annealed with 1-butanol vapor. Systematical studies demonstrated that the PEA₂PbI₄/MAPbI₃ bilayer thin films post-annealed with 1-butanol vapor possessed superior crystallinity and boosted charge transport. Moreover, compared to perovskite photovoltaics (PPVs) based on the 3D MAPbI₃ thin film, PPVs based on the PEA₂PbI₄/MAPbI₃ bilayer thin film exhibited increased built-in potential, suppressed charge carrier recombination, and boosted charge transport. As a result, we observed high performance, in terms of power conversion efficiency, photodetectivity, and stability, from PPVs based on the PEA₂PbI₄/MAPbI₃ bilayer thin films post-treated with 1-butanol vapor annealing. For example, over 22% power conversion efficiency and dramatically enhanced stability were observed from perovskite solar cells. Moreover, over 10¹⁴ Jones detectivity and a large linear dynamic range of 167 dB were observed from perovskite photodetectors. These

results demonstrated that we have developed a simple method to approach high-performance PPVs.

4. EXPERIMENTAL SECTION

4.1. Materials. Methylammonium iodide (MAI, 99.9%) was purchased from GreatCell Solar. Phenethylammonium iodide (PEAI, 99.9%) was purchased from Sigma-Aldrich. Lead iodide (PbI₂, 99.9985%, metals basis) was purchased from Alfa Aesar. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), bathocuproine (BCP, 99.99%), fullerene (C₆₀, 99.5%), bathocuproine, methylamine (MA) (33 wt % in absolute ethanol), anhydrous acetonitrile (ACN, 99.8%), isopropanol (99.5%), 1-butanol (99.8%), γ -butyrolactone (GBL, 99%), and toluene (99.8%) were purchased from Sigma-Aldrich. All chemicals were used as received without any further purification.

4.2. Preparation and Characterization of Perovskite Thin Films. The MAPbI₃ single crystal was grown, and the MAPbI₃ ACN solution was followed from previous reports.^{29,35} The preparation procedures of the PEA₂PbI₄/MAPbI₃ bilayer thin films are schematically displayed in Scheme S1. A PEA 1-butanol solution (80 μL , 1 mg/mL) was dropped on the surface of the 3D MAPbI₃ thin film and kept for 10 s before starting the spin-coating process (6000 RPM for 30 s). The resultant thin films were thermally annealed at 100 $^{\circ}\text{C}$ under 1-butanol vapor for 5 min.

The XRD patterns, ultraviolet–visible (UV–vis) absorption spectra, PL spectra, top-view SEM images, and thicknesses of the perovskite thin films were characterized as described in our previous publications.^{6,7,35–38}

4.3. Fabrication and Characterization of Photovoltaic Devices. The procedures of the PPV fabrication and characterization are the same as previously reported.^{6,7,35–38} The device area was measured to be 0.043 cm². A specific wavelength was obtained using a spectrum filter for giving a monochromatic light at a wavelength (λ) of 500 nm with a light intensity of 0.28 mW cm⁻². The transient photocurrent (TPC) measurement was described as reported previously.^{36–38} The temporal photocurrent response time of PPDs was performed on a homemade setup using an optical chopper with a wavelength of 532 nm laser pulse at a frequency of 2 kHz. Note that the speed of the optical chopper frequency or duty cycle is in the range of nanoseconds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.1c15735>.

Preparation of perovskite thin films; characterization of perovskite thin films; characterization of perovskite solar

cells, and characterization of perovskite photodetectors (PDF)

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Notes

The authors declare no competing financial interest.

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