


 Cite this: *RSC Adv.*, 2026, **16**, 16865

# Surface engineering of SnO<sub>2</sub> for improved perovskite/SnO<sub>2</sub> photodetectors

 Jing Cai,<sup>a</sup> Guipeng Li,<sup>b</sup> Yulong Ying,<sup>c</sup> Hongping Li,<sup>\*d</sup> Ahmad Fairuz Omar,<sup>a</sup> Marzaini Rashid<sup>\*a</sup> and Mingming Chen<sup>\*b</sup>

Lead halide perovskite (LHP) heterojunctions have proven to be promising for achieving low-cost and efficient photodetection. However, the remarkable interfacial non-radiative recombination severely deteriorated the performance of the resulting devices. Herein, surface engineering of SnO<sub>2</sub> with ammonium tetrathiotungstate ((NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub>) has been proposed to effectively passivate the interfacial defects at the LHP CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/SnO<sub>2</sub> interface to fabricate high-performance photodetectors (PDs). Experimental and theoretical studies showed that the surface engineering with (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> resulted in S substituting for oxygen lattice of SnO<sub>2</sub>, which passivated the surface oxygen vacancies of SnO<sub>2</sub>. Further studies have shown that the S atoms at the surface of SnO<sub>2</sub> further suppressed the I vacancies and Pb vacancies at the bottom surface of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. Finally, improved CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/SnO<sub>2</sub> PDs with the responsivity and detectivity of 0.41 A W<sup>-1</sup> and 5 × 10<sup>12</sup> Jones, respectively, at zero bias, have been demonstrated. The results presented in this work provide promising pathways to effectively passivate the interfacial defects of LHP/SnO<sub>2</sub> heterojunctions for achieving efficient photodetection in the future.

 Received 31st December 2025  
 Accepted 20th March 2026

DOI: 10.1039/d5ra10121b

[rsc.li/rsc-advances](https://rsc.li/rsc-advances)

## Introduction

Photodetectors (PDs), which can directly convert photons into electrical charge, are a fundamental component of various modern photodetection and imaging systems, such as digital imaging and hyperspectral sensing.<sup>1–5</sup> Recently, halide lead perovskites (LHPs) (ABX<sub>3</sub>, where A is CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> (MA<sup>+</sup>), HC(NH<sub>2</sub>)<sub>2</sub><sup>+</sup> (FA<sup>+</sup>); B is the Pb<sup>2+</sup>; X is the Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>) have attracted tremendous attention in the optoelectronics community because of their superior optoelectrical properties including high absorption coefficient, long charge carrier diffusion length, and long charge carrier lifetime.<sup>6</sup> Benefiting from these advantages, LHPs have been regarded as potential candidates for realizing low-cost and efficient light harvesting and photodetection.<sup>7</sup> Notably, various kinds of LHP PDs, including narrowband, broadband, and wavelength-selective PDs, have been fabricated recently.<sup>8,9</sup> Benefiting from various advantages, such as a combination of optoelectrical properties of both semiconductors and being free from the need for controlled n- and p-type doping of specific materials,<sup>10–13</sup> LHP heterojunctions fabricated by preparing LHP and a different

semiconductor in sequence have been considered as essential building blocks for fabricating efficient and cost-effective self-powered PDs.<sup>14,15</sup>

Recently, the rapid progresses of power conversion efficiency of LHP solar cells have motivated the explorations of advanced carrier transport layers.<sup>16</sup> It is worth noting that wide bandgap semiconductor tin oxide (SnO<sub>2</sub>) has been widely employed to fabricate efficient LHP solar cells recently, benefiting from its high electron mobility, deep conduction band, and low-temperature processabilities.<sup>17</sup> Meanwhile, the construction of efficient PDs based on various LHP/SnO<sub>2</sub> heterojunctions has been further explored.<sup>18</sup> Similar to light harvesting, efficient photodetection can be readily achieved through a combination of the efficient absorption of photons and the efficient collection of excess carriers. Benefiting from ion doping-assisted suppression of point defects and seed layer-assisted nucleation-induced suppression of grain defects, the bulk defects of LHP thin films have been remarkably suppressed.<sup>19,20</sup> However, the interfacial defects induced non-radiative recombination have severely lowered the efficiency of carrier collection, greatly limiting the performance of LHP/SnO<sub>2</sub> heterojunction PDs.<sup>21,22</sup> In general, the interfacial defects consist of the surface defects of the buried layer and the deposited layer. In the case of the LHP/SnO<sub>2</sub> heterojunctions, the SnO<sub>2</sub> thin films prepared with various techniques have suffered from the natural surface oxygen vacancies (V<sub>OS</sub>).<sup>22</sup> In addition, halide vacancies and lead vacancies have been evidenced at the bottom surface of LHPs owing to the weak bonding between LHPs and SnO<sub>2</sub>.<sup>23</sup> It has been widely reported

<sup>a</sup>School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia. E-mail: marzaini@usm.my

<sup>b</sup>Department of Microelectronics, Jiangsu University, Zhenjiang, Jiangsu 212013, China. E-mail: andychain@live.cn

<sup>c</sup>School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou, 310018, China

<sup>d</sup>School of Materials Science and Engineering, Jiangsu University, Zhenjiang, Jiangsu 212013, China. E-mail: hpli@ujs.edu.cn


that both surface defects deteriorated the performance of LHP/SnO<sub>2</sub> heterojunction devices.<sup>24</sup> Very recently, a great amount of effort has been devoted to suppressing the interfacial defects for fabricating improved LHP/SnO<sub>2</sub> heterojunction PDs.<sup>25</sup> However, the existing literatures mostly focused on either passivating the surface V<sub>OS</sub> of SnO<sub>2</sub> thin films or suppressing the halide vacancies and lead vacancies at the bottom surface of LHPs.<sup>26,27</sup> For example, inorganic dielectric layers have been employed to passivate the surface V<sub>OS</sub> of SnO<sub>2</sub> thin films.<sup>28</sup> Besides, various organic groups have been explored, but mainly suppress the halide vacancies and lead vacancies at the bottom surface of LHP thin films.<sup>29</sup> Practically, effective suppression of surface defects of both materials is fundamental for improving the performance of LHP/SnO<sub>2</sub> heterojunction PDs, while the related studies have seldom been reported so far.

Herein, surface engineering of SnO<sub>2</sub> with ammonium tetrathiotungstate ((NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub>) has been proposed to realize an effective suppression of surface V<sub>OS</sub> of SnO<sub>2</sub> and iodine vacancies (V<sub>I</sub>) and lead vacancies (V<sub>Pb</sub>) at the bottom surface of MAPbI<sub>3</sub>. It has been shown that the surface V<sub>OS</sub> of SnO<sub>2</sub> were effectively passivated *via* the sulfur (S) substitution for oxygen (O) lattice. In addition, the S atoms at the surface of SnO<sub>2</sub> further suppressed the V<sub>I</sub> and V<sub>Pb</sub> defects at the bottom surface of MAPbI<sub>3</sub>. Collectively, performance-improved MAPbI<sub>3</sub>/SnO<sub>2</sub> PDs with the responsivity and detectivity as high as 0.41 A W<sup>-1</sup> and 5 × 10<sup>12</sup> Jones, respectively, at the zero bias, have been demonstrated.

## Results and discussions

The MAPbI<sub>3</sub>/SnO<sub>2</sub> PDs were fabricated by spin-coating SnO<sub>2</sub> and MAPbI<sub>3</sub> thin films in sequence on an ITO substrate (Fig. 1a) (see experiments in SI for details). The treatment of surface engineering of SnO<sub>2</sub> was realized by adding (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> into SnO<sub>2</sub> aqueous solution, where the surface V<sub>OS</sub> of SnO<sub>2</sub> were passivated through the S substitution during stirring. The morphological and structural properties of samples were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. The suppression of surface V<sub>O</sub> defects in SnO<sub>2</sub> and V<sub>Pb</sub> of MAPbI<sub>3</sub> has been verified through steady-state and transient photoluminescence (PL), X-ray photoelectron spectroscopy (XPS) characterizations, and density functional theory (DFT) calculations.

Structure and elements analysis have confirmed the crystallization of SnO<sub>2</sub> after spin-coating of pure SnO<sub>2</sub> and SnO<sub>2</sub>/(NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> aqueous solutions (Fig. S1–S2, SI). Fig. 1b and c show the typical SEM images of SnO<sub>2</sub> and S-SnO<sub>2</sub> thin films. It shows that the S-SnO<sub>2</sub> thin films exhibit an improved morphology in terms of improved compactness and uniformity, while the SnO<sub>2</sub> thin films show a rough surface with notable gaps. This suggests that the (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> additive benefits the preparation of high-quality SnO<sub>2</sub> thin films from nanoparticles. Due to the small thickness and limited resolution of the SEM technique, the thickness of SnO<sub>2</sub> and S-SnO<sub>2</sub> thin films was not obtained, but has been estimated as ~10 nm from the previous reports.<sup>30</sup> Notably, the compact and uniform morphology of S-SnO<sub>2</sub> thin films exhibits a reduction of carrier scattering effect.

As revealed from current–voltage (*I*–*V*) measurements (Fig. S3, SI), the S-SnO<sub>2</sub> thin films feature a reduced resistivity. As a result, the carrier collection at the MAPbI<sub>3</sub>/SnO<sub>2</sub> interfaces is expected to be improved.

Fig. 1d–g present the SEM images of MAPbI<sub>3</sub> thin films spin-coated on SnO<sub>2</sub> and S-SnO<sub>2</sub> thin films. As shown, both samples exhibit a similar morphology with comparable grain size, compactness, and thickness. Specifically, the grain sizes and thickness of both samples were characterized as around 450 ± 32 nm (Fig. 1d and e) and 230 nm (Fig. 1f and g), respectively. This suggests that surface engineering of SnO<sub>2</sub> with (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> seems not to influence the growth processes of MAPbI<sub>3</sub> thin films.

Structural and optical properties measurements were carried out to further compare the quality of MAPbI<sub>3</sub> thin films prepared on SnO<sub>2</sub> and S-SnO<sub>2</sub> thin films, and the results are shown in Fig. 2. It shows that both MAPbI<sub>3</sub> thin films exhibit similar XRD patterns (Fig. 2a), which can be indexed into the orthorhombic phase. Careful analysis shows that both MAPbI<sub>3</sub> thin films exhibit similar crystalline quality from the XRD peaks' positions and full width at half maximums (FWHMs, Table S1, SI). Such a claim can be supported from small differences in their steady and transient PL spectra (Fig. 2b). As shown, the PL intensity and carrier recombination processes of both MAPbI<sub>3</sub> thin films are almost same. Collectively, surface engineering with the (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> has improved the morphology of SnO<sub>2</sub> thin films, while it has neglected roles in subsequent crystallization of MAPbI<sub>3</sub> thin films.

To verify the suppression of surface V<sub>OS</sub>, XPS measurements on the SnO<sub>2</sub> thin films were performed. Notably, the XPS method has shown strong effectiveness in analyzing surface chemical composition.<sup>31,32</sup> Fig. 3a illustrates the core-level spectra of O 1s of SnO<sub>2</sub> and S-SnO<sub>2</sub> thin films. Both spectra can be fitted into three peaks (peak I, II, and III), which correspond to various states of O at the SnO<sub>2</sub> surface. As can be seen, the binding energies are observed at 530.5 eV, 531.3 eV, and 532.0 eV, which can be attributed to lattice O, V<sub>O</sub>, and adsorbed oxhydryl (OH<sup>-</sup>), respectively.<sup>33</sup> Notably, the concentration of various components can be semiquantitatively evaluated from the relative intensities of corresponding XPS peaks.<sup>33</sup> Accordingly, it can be concluded that S-SnO<sub>2</sub> thin films show a reduced surface V<sub>O</sub> from the decreased intensity of peak II compared to SnO<sub>2</sub> thin films. Further observations suggest that the reduction of surface V<sub>OS</sub> is probably caused by the S substituting for O in S-SnO<sub>2</sub> thin films. On the one hand, a remarkable peak can be observed in S 2p XPS spectrum (Fig. 3b), which verifies the successful doping of S in S-SnO<sub>2</sub> thin films. On the other hand, the binding energies of Sn 3d in S-SnO<sub>2</sub> thin films redshift by around 0.3 eV compared to those in SnO<sub>2</sub> thin films (Fig. 3c). This is attributed to the increased electron density around Sn atoms,<sup>34</sup> which well correlates to the formation of the Sn–S bond in the current situation.

The above observations indicate that interface engineering with (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> resulted in a doping of S atoms, which suppressed the surface V<sub>OS</sub> in S-SnO<sub>2</sub> thin films. However, it is difficult to reveal the doping processes at this stage, but can be expected as follows:



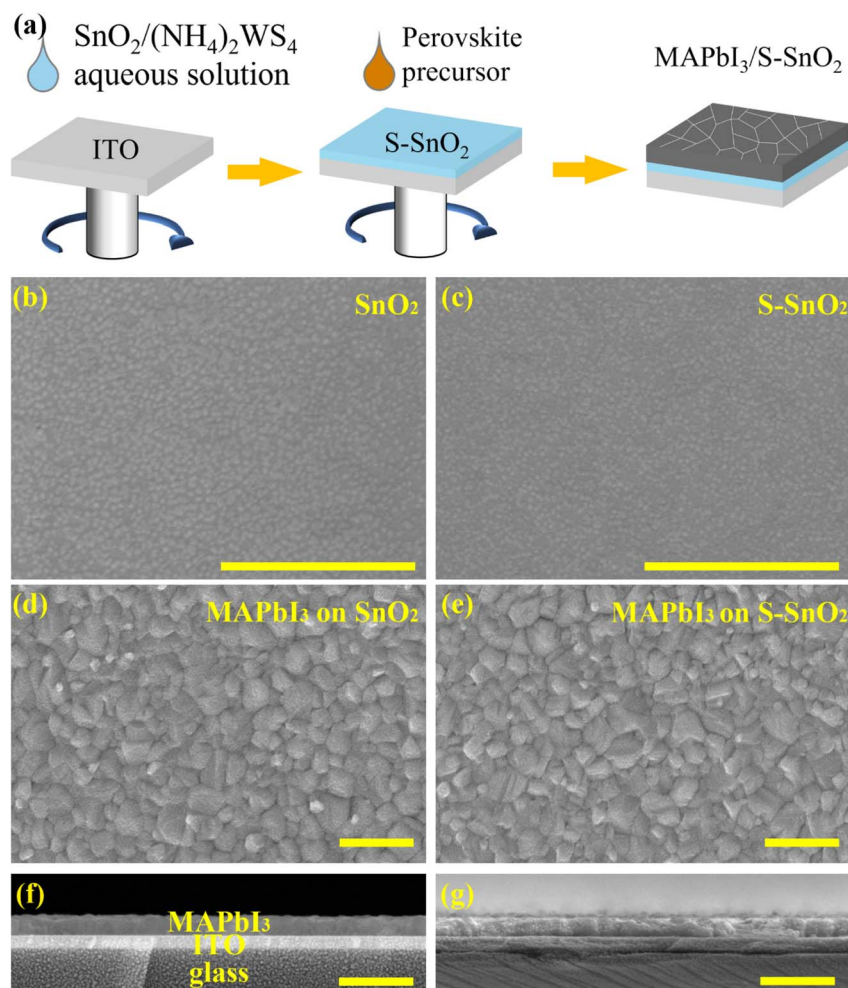
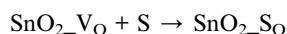


Fig. 1 Morphology of  $\text{SnO}_2$  and  $\text{MAPbI}_3$  thin films. (a) Scheme of experimental details for preparing  $\text{MAPbI}_3/\text{S-SnO}_2$  heterojunctions. SEM images of (b)  $\text{SnO}_2$ , (c)  $\text{S-SnO}_2$ , (d and f)  $\text{MAPbI}_3$  thin films grown on  $\text{SnO}_2$ , and (e and g)  $\text{MAPbI}_3$  thin films grown on  $\text{S-SnO}_2$ .



where  $\text{SnO}_2\text{-V}_\text{O}$  is the  $\text{SnO}_2$  with a surface  $\text{V}_\text{O}$ ,  $\text{SnO}_2\text{-S}_\text{O}$  is the  $\text{SnO}_2$  with S substituting for O lattice. Herein, to better understand the mechanisms of suppression of surface  $\text{V}_\text{O}\text{S}$  by S doping, DFT calculations were carried out. As reported before,

the probability of S substitution for surface O lattice ( $\text{S}_\text{O}$ ) can be revealed from their formation energies ( $\Delta E$ ),<sup>35</sup> which can be calculated from the eqn (1):

$$\Delta E(\text{SnO}_2\text{-S}_\text{O}) = E(\text{SnO}_2\text{-S}_\text{O}) - [E(\text{SnO}_2\text{-V}_\text{O}) + E(\text{S})] \quad (1)$$

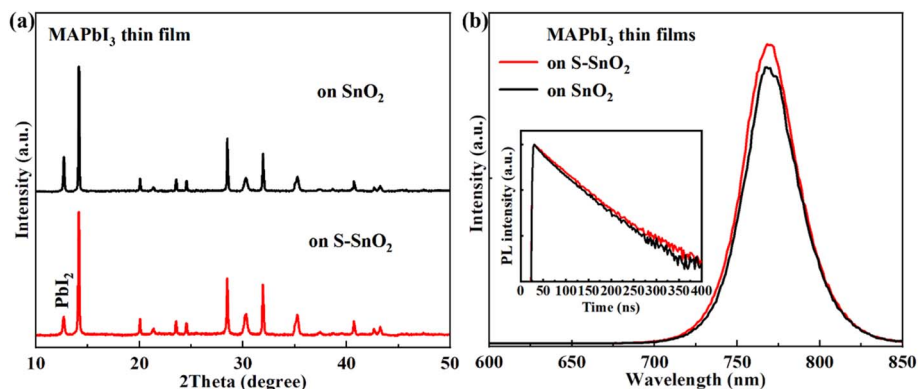


Fig. 2 Structural and optical properties of  $\text{MAPbI}_3$  thin films grown on  $\text{SnO}_2$  and  $\text{S-SnO}_2$ . (a) XRD and (b) PL. The inset in (b) shows the TRPL.



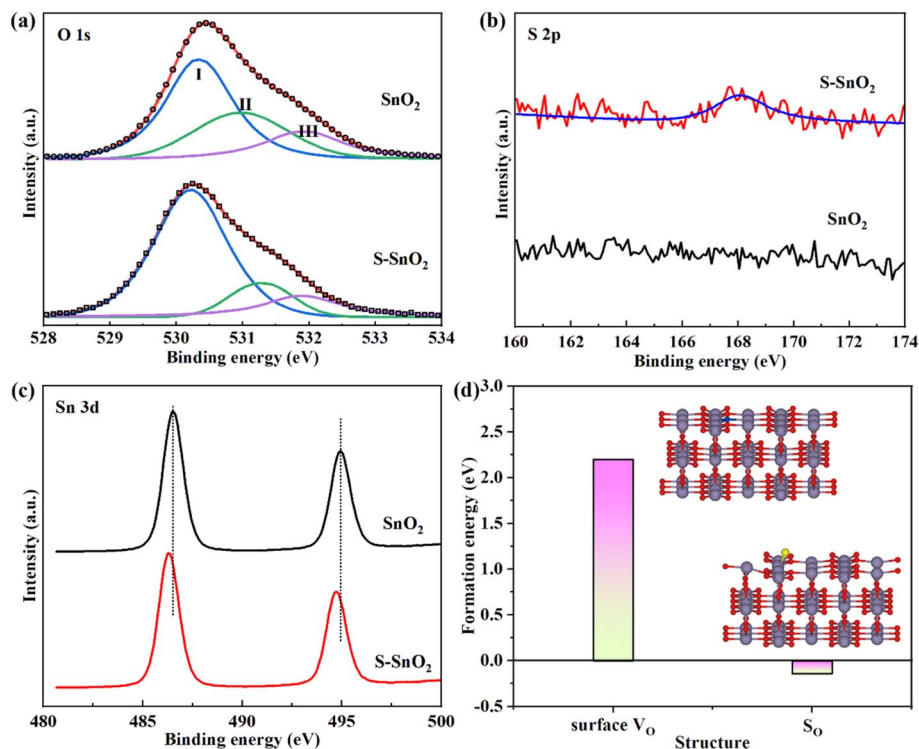


Fig. 3 Passivation of surface  $V_O$ s of  $SnO_2$  by S atoms. (a–c) XPS data of (a) O, (b) S, and (c) Sn atoms. (d) Formation energies of surface  $V_O$ s and S substituting for O of  $SnO_2$ . The inset in (d) indicates the corresponding supercells, where red, gray, blue, and yellow balls are O, Sn,  $V_O$ , and S, respectively.

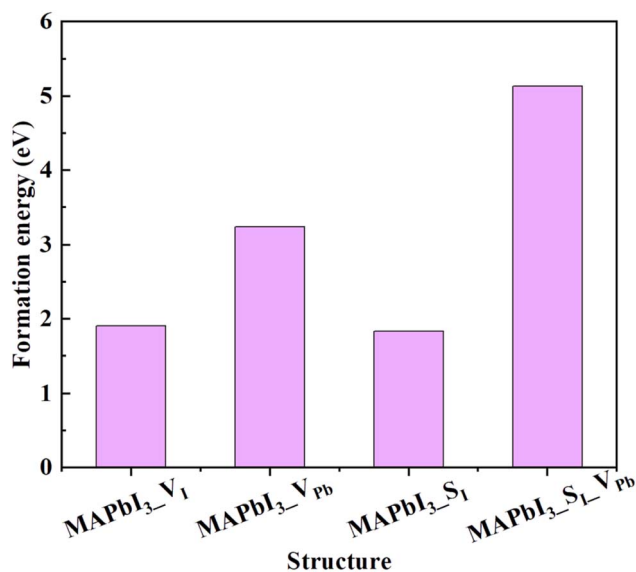


Fig. 4 Formation energies of  $V_I$ ,  $V_{Pb}$ , S substituting for I, and S substituting for I with a  $V_{Pb}$  nearby of  $MAPbI_3$ . The corresponding supercells are depicted in Fig. S4 (SI). The formation energies were calculated using formulas similar to eqn (1).

where  $E(SnO_2-S_O)$ ,  $E(SnO_2-V_O)$ , and  $E(S)$  are the total energies of the supercell with S substitution for surface O and that with a surface  $V_O$ , and the energy of individual S atom, respectively. The formation energy of  $SnO_2-V_O$  structure ( $\Delta E(SnO_2-V_O)$ ) was

calculated with a similar scenario. Fig. 3d depicts the formation energies of  $SnO_2$  with a surface  $V_O$  and S substitution for surface O. It can be seen that the formation energy of surface  $V_O$  is as high as 2.198 eV. This suggests that the high-density surface  $V_O$  (Fig. 3a) cannot be related to thermodynamic effects, but might be attributed to mechanical effects between the nanoparticles or hydrogen bonding in the solvent environment. Notably, the formation energy of S substitution for surface O was calculated as low as  $-0.141$  eV. This shows that the  $S_O$  structure is thermally preferred, which demonstrates the effective suppression of surface  $V_O$ s of  $SnO_2$  through the surface engineering with the  $(NH_4)_2WS_4$ .

It has been noticed that S atoms on the  $SnO_2$  surface showed a strong electrostatic interaction with Pb ions of  $MAPbI_3$  compared to O of  $SnO_2$ .<sup>36</sup> In this case, the interfacial S atoms are expected to fill the  $V_I$  and further suppress the formation of  $V_{Pb}$  at the bottom surface of  $MAPbI_3$  thin films. Since the small penetration depth of X-ray, the local chemical states of Pb and I atoms at the  $MAPbI_3/SnO_2$  interface cannot be experimentally explored from XPS techniques. To demonstrate the hypotheses, the formation energies of  $MAPbI_3$  with a  $V_I$  ( $MAPbI_3-V_I$ ),  $MAPbI_3$  with a  $V_{Pb}$  ( $MAPbI_3-V_{Pb}$ ),  $MAPbI_3$  with a S atom substituting for I lattice ( $MAPbI_3-S_I$ ), and  $MAPbI_3-S_I$  with a  $V_{Pb}$  nearby S ( $MAPbI_3-S_I-V_{Pb}$ ) (Fig. S4, SI) were calculated, and the results are provided in Fig. 4. It shows that the  $MAPbI_3-S_I$  structure shows a reduced formation energy (1.84 eV) compared to  $MAPbI_3-V_I$  (1.91 eV), and the  $MAPbI_3-S_I-V_{Pb}$  exhibits a reduced formation energy (3.25 eV) compared to  $MAPbI_3-V_{Pb}$



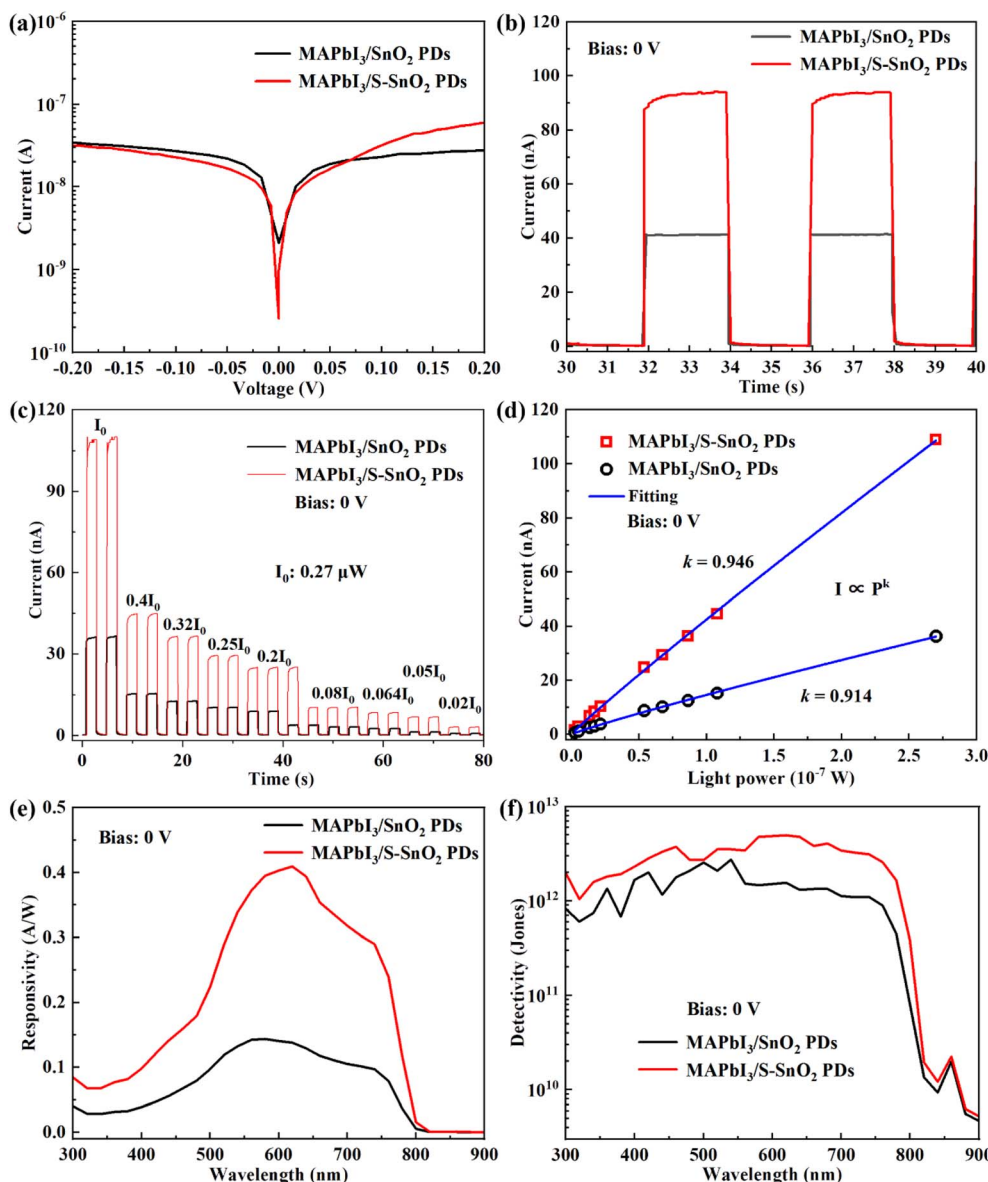


Fig. 5 Performance of MAPbI<sub>3</sub>/SnO<sub>2</sub> PDs. (a)  $I$ - $V$  curves captured in dark. (b)  $I$ - $t$  curves captured under pulsed illumination. (b and c)  $I$ - $t$  curves and photocurrent captured under different light powers. Data in d were extracted from c. (e) Responsivity. (f) Detectivity.

(5.14 eV). This suggests that the S atoms at the surface of SnO<sub>2</sub> thin films have remarkable potential to suppress the  $V_i$  and  $V_{pb}$  defects at the bottom surface of MAPbI<sub>3</sub> thin films.

After sputtering Au electrodes, MAPbI<sub>3</sub>/SnO<sub>2</sub> heterojunction PDs were fabricated (Fig. S5, SI). As shown in Fig. S6 (SI), among various concentrations, engineering SnO<sub>2</sub> NPs with 1.0 mg mL<sup>-1</sup> of (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> produced the optimal MAPbI<sub>3</sub>/S-SnO<sub>2</sub> PDs, resulting in the highest photocurrent. Accordingly, the performance of MAPbI<sub>3</sub>/S-SnO<sub>2</sub> PDs, prepared with 1.0 mg mL<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> engineering, is examined in detail below. Fig. 5a illustrates the  $I$ - $V$  curves of MAPbI<sub>3</sub>/SnO<sub>2</sub> and MAPbI<sub>3</sub>/S-SnO<sub>2</sub> PDs captured in the dark. It shows that the MAPbI<sub>3</sub>/S-SnO<sub>2</sub> PDs exhibit reduced current under reverse bias and reduced turn-on voltage under forward bias. As shown in Fig. 1 and 2, the MAPbI<sub>3</sub> thin films prepared on SnO<sub>2</sub> and S-SnO<sub>2</sub> exhibit a similar crystalline quality.

Thus, the reduced reverse current and turn-on voltage can be attributed to the suppression of interfacial defects at the MAPbI<sub>3</sub>/S-SnO<sub>2</sub> interface, as discussed above.

Fig. 5b shows the current-time ( $I$ - $t$ ) curves of MAPbI<sub>3</sub>/SnO<sub>2</sub> and MAPbI<sub>3</sub>/S-SnO<sub>2</sub> PDs at zero bias with 540 nm illumination switched on and off. It can be seen that both devices show excellent on-off switching performance. Notably, the MAPbI<sub>3</sub>/S-SnO<sub>2</sub> PDs show an improved photocurrent, which increased by around 2.2 times compared to MAPbI<sub>3</sub>/SnO<sub>2</sub> PDs. According to above discussions, this should be caused by the suppressed interfacial non-radiative recombination at MAPbI<sub>3</sub>/S-SnO<sub>2</sub> interfaces. Further studies suggest that both devices exhibit nearly a linear response to light power. As shown in Fig. 5c and d, the photocurrents of MAPbI<sub>3</sub>/SnO<sub>2</sub> and MAPbI<sub>3</sub>/S-SnO<sub>2</sub> PDs nearly scale linearly with light power from 10<sup>-9</sup> W to 10<sup>-7</sup> W,



Table 1 Comparison of photodetection performance of MAPbI<sub>3</sub>/SnO<sub>2</sub> heterojunction PDs and related devices reported before

Device	Bias (V)	Responsivity (A/W)	Detectivity (Jones)	Ref.
Spiro-OMeTAD/FAPb(I/Br) <sub>3</sub> /SnO <sub>2</sub>	1.0	0.0438	$3.56 \times 10^{13}$	37
Spiro-OMeTAD/MAFAPb(Br/I) <sub>3</sub> /SnO <sub>2</sub>	1.0	0.0722	$4.67 \times 10^{13}$	38
SnO <sub>2</sub> /MAPbI <sub>3</sub> /MoO <sub>3</sub>	0	0.0509	$2.23 \times 10^{12}$	39
CsCu <sub>2</sub> I <sub>3</sub> /GaN	0	0.10634	$9.24 \times 10^{11}$	40
MAPbI <sub>3</sub> /ZnO	7	2.73	$1.09 \times 10^{12}$	41
C <sub>60</sub> /MAPbI <sub>3</sub> /GaN	0	0.198	$7.96 \times 10^{12}$	42
TiO <sub>2</sub> /MAPbI <sub>3</sub>	-0.8	0.405	$2.07 \times 10^{11}$	43
PEDOT:PSS/MAPbI <sub>3</sub> /PTB7-Th:COTIC-4F	-0.5	0.58	$1.64 \times 10^{12}$	44
MAPbI <sub>3</sub> /SnO <sub>2</sub> @r-PMO <sub>11</sub> V	3	0.039	$9.3 \times 10^{10}$	45
MAPbI <sub>3</sub> /S-SnO <sub>2</sub>	0	0.41	$4.6 \times 10^{12}$	This work

suggesting that MAPbI<sub>3</sub>/SnO<sub>2</sub> heterojunction PDs can be used to detect the light power.

The performance of MAPbI<sub>3</sub>/SnO<sub>2</sub> and MAPbI<sub>3</sub>/S-SnO<sub>2</sub> PDs is further studied from the responsivity and detectivity, and the results are shown in Fig. 5c and d. As reported before, the responsivity ( $R$ ) and detectivity ( $D^*$ ) can be calculated from eqn (2) and (3) provided below:

$$R = \frac{I_{\text{ph}} - I_{\text{dark}}}{P \times S} \quad (2)$$

$$D^* = \frac{R}{\sqrt{2eI_{\text{dark}}/S}} \quad (3)$$

where  $I_{\text{ph}}$  and  $I_{\text{dark}}$  are the photocurrent and dark current,  $P$  is the light power density (in  $\text{W cm}^{-2}$ ),  $S$  is the device area (the area of the top Au electrode,  $0.01 \text{ mm}^2$ ),  $e$  is the electric charge ( $1.6 \times 10^{-19} \text{ C}$ ). As depicted in Fig. 5e and f, the photoresponsivity and detectivity of MAPbI<sub>3</sub>/SnO<sub>2</sub> PDs are  $0.14 \text{ A W}^{-1}$  and  $2 \times 10^{12}$  Jones, respectively, at the zero bias, which increased by around 2.9 times ( $0.41 \text{ A W}^{-1}$ ) and 2.3 times ( $4.6 \times 10^{12}$  Jones) for MAPbI<sub>3</sub>/S-SnO<sub>2</sub> PDs. The improved

photodetection performance of MAPbI<sub>3</sub>/S-SnO<sub>2</sub> PDs is mainly attributed to the suppressed interfacial non-radiative recombination, which benefits from the effective interfacial passivation induced by the surface engineering with  $(\text{NH}_4)_2\text{WS}_4$  as evidenced above. Table 1 summarizes a comparison of the photodetection performance of the MAPbI<sub>3</sub>/S-SnO<sub>2</sub> PDs shown herein and related PDs reported before, highlighting the critical roles of surface engineering with  $(\text{NH}_4)_2\text{WS}_4$  in improving the performance of MAPbI<sub>3</sub>/SnO<sub>2</sub> heterojunction PDs.

Further studies reveal that surface engineering of SnO<sub>2</sub> with  $(\text{NH}_4)_2\text{WS}_4$  improved the stability of photodetection. As shown in Fig. 6a and b, the photocurrent of MAPbI<sub>3</sub>/SnO<sub>2</sub> PDs decreases to 85% of the initial value under pulsed illumination (Fig. 6a) and 60% under steady illumination (Fig. 6b) over 3600 s. In comparison, the photocurrent slightly decreases (2% and 10%) in MAPbI<sub>3</sub>/S-SnO<sub>2</sub> PDs. Generally, the interfacial non-radiative recombination induces substantial thermal effects under illumination,<sup>46</sup> which account for the inferior stability observed in MAPbI<sub>3</sub>/SnO<sub>2</sub> PDs. Thus, the improved stability of photodetection of MAPbI<sub>3</sub>/S-SnO<sub>2</sub> mainly benefits from the effective interfacial passivation as discussed above.

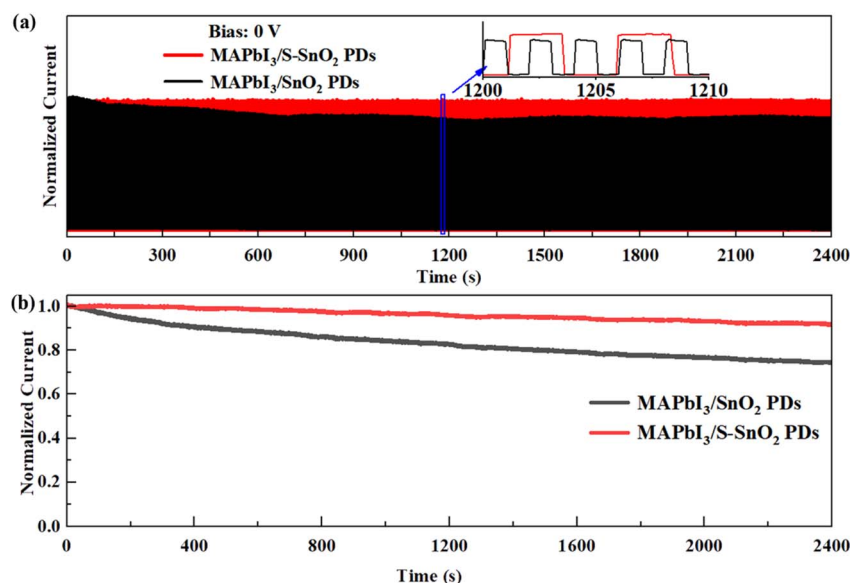


Fig. 6 Stability of photodetection of MAPbI<sub>3</sub>/SnO<sub>2</sub> PDs.  $I-t$  curves captured (a) under pulsed illumination and (b) steady illumination.



In conclusion, surface engineering of SnO<sub>2</sub> with (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> has been demonstrated to effectively passivate the interfacial defects to fabricate improved MAPbI<sub>3</sub>/SnO<sub>2</sub> PDs. It has been shown that the surface engineering with (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub> resulted in S substituting for O lattice of SnO<sub>2</sub>, which passivated the surface V<sub>OS</sub> of SnO<sub>2</sub>. Meanwhile, theoretical studies suggested that the S atoms at the surface of SnO<sub>2</sub> further suppressed the V<sub>I</sub> and V<sub>Pb</sub> at the bottom surface of MAPbI<sub>3</sub>. Accordingly, the interfacial non-radiative recombination has been suppressed. On this basis, improved MAPbI<sub>3</sub>/SnO<sub>2</sub> PDs have been fabricated, where the responsivity and detectivity of 0.41 A W<sup>-1</sup> and 5 × 10<sup>12</sup> Jones at the zero bias have been demonstrated. The results shown in this work pave the way for efficiently passivating the interfacial defects of LHP/SnO<sub>2</sub> heterojunctions in the future.

## Conflicts of interest

The authors declare no conflict of interest.

## Data availability

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Supplementary information (SI): experiments, and supporting figures including XRD and XPS results of SnO<sub>2</sub> and S-SnO<sub>2</sub> thin films, I–V curves of Au/SnO<sub>2</sub> (S-SnO<sub>2</sub>)/ITO structures, supercells of MAPbI<sub>3</sub> containing various defects, and a photo image of MAPbI<sub>3</sub>/SnO<sub>2</sub> PDs, statistical results of dark current and photocurrent of MAPbI<sub>3</sub>/SnO<sub>2</sub> PDs treated with different (NH<sub>4</sub>)<sub>2</sub>WS<sub>4</sub>, and supporting Tables for comparison of crystallinity of MAPbI<sub>3</sub> thin films prepared on SnO<sub>2</sub> and S-SnO<sub>2</sub>. See DOI: <https://doi.org/10.1039/d5ra10121b>.

## References

- U. Khulal, J. Zhao, W. Hu and Q. Chen, Nondestructive quantifying total volatile basic nitrogen (TVB-N) content in chicken using hyperspectral imaging (HSI) technique combined with different data dimension reduction algorithms, *Food Chem.*, 2016, **197**, 1191–1199.
- J. Sun, S. Jiang, H. Mao, X. Wu and Q. Li, Classification of Black Beans Using Visible and Near Infrared Hyperspectral Imaging, *Int. J. Food Prop.*, 2016, **19**(8), 1687–1695.
- Q. Chen, W. Hu, J. Su, H. Li, Q. Ouyang and J. Zhao, Nondestructively sensing of total viable count (TVC) in chicken using an artificial olfaction system based colorimetric sensor array, *J. Food Eng.*, 2016, **168**, 259–266.
- L. Wan, H. Li, C. Li, A. Wang, Y. Yang and P. Wang, Hyperspectral Sensing of Plant Diseases: Principle and Methods, *Agronomy*, 2022, **12**(6), 1451.
- Y. Xu, M. M. Hassan, A. S. Sharma, H. Li and Q. Chen, Recent advancement in nano-optical strategies for detection of pathogenic bacteria and their metabolites in food safety, *Crit. Rev. Food Sci. Nutr.*, 2023, **63**(4), 486–504.
- R. Wang, M. Mujahid, Y. Duan, Z.-K. Wang, J. Xue and Y. Yang, A Review of Perovskites Solar Cell Stability, *Adv. Funct. Mater.*, 2019, **29**(47), 1808843.
- Z. Y. Zhang, L. Sun and G. P. Wang, Lateral Perovskite Single-Crystal Capacitors for Self-Powered Photodetection, *Adv. Electron. Mater.*, 2023, **9**(4), 2201318.
- X. Shen, S. Yang, M. Chen, J. Su, J. Cai, P. Cheng, Y. Liu, Q. Wang and D. Cao, Interfacial Engineering with Aluminum Oxide toward an Improved Self-Powered Narrowband Visible-Light Photodetection in Lead Halide Perovskite CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub>/p-Si Heterojunctions, *Adv. Mater. Interfaces*, 2022, **9**(14), 2102305.
- L.-J. Feng, Y.-Y. Zhao, R.-Y. Song and X.-W. Lei, Three homologous 1D lead halide perovskites with broadband white-light emissions, *Inorg. Chem. Commun.*, 2022, **136**, 109146.
- P. C. Kumar, S. Mohanty, J. Panda, S. Das, S. Supriya, D. Alagarasan and R. Naik, Enhanced photoresponse in a Ag<sub>2</sub>S/In<sub>2</sub>Se<sub>3</sub> heterojunction based visible light photodetector, *RSC Adv.*, 2025, **15**(18), 14518–14531.
- L. Mahapatra, S. Supriya, P. C. Kumar, D. Alagarasan, C. Sripan and R. Naik, Increase in photo sensitivity and detectivity of Bi/Sb<sub>35</sub>Se<sub>30</sub> heterostructure films upon time-dependent laser irradiation for photodetection, *Surf. Interfaces*, 2025, **72**, 107091.
- K. Manjunatha, D. Alagarasan, S. Das, R. Ganesan, R. Naik, D. Purohit and M. Ramudu, Influence of substrate temperature on SnSe<sub>2</sub>/TiO<sub>2</sub> heterostructure for photodetector applications, *Sens. Actuators, A*, 2025, **391**, 116641.
- G. Mallick, P. C. Kumar, R. Naik and R. Biswal, Enhanced Photoresponse from Ag/Bi<sub>2</sub>Se<sub>3</sub> Heterostructure Thin Films under Thermal Annealing, *ACS Appl. Electron. Mater.*, 2025, **7**(12), 5583–5598.
- S. Kumaresan, I. Kathiravan, V. Vijendran and J. Balasundaram, Inorganic hole transport layer for lead free bismuth halide perovskite for photovoltaic device, *Opt. Mater.*, 2024, **154**, 115722.
- J. Haddad, B. Krogmeier, B. Klingebiel, L. Krueckemeier, S. Melhem, Z. Liu, J. Huepkes, S. Mathur and T. Kirchartz, Analyzing Interface Recombination in Lead-Halide Perovskite Solar Cells with Organic and Inorganic Hole-Transport Layers, *Adv. Mater. Interfaces*, 2020, **7**(16), 2000366.
- K. Ahmad and R. A. Khan, Improved photovoltaic performance of lead halide perovskite solar cells using spiro-OMeTAD plus CNTs as hole transport layer, *J. Mater. Sci. Mater. Electron.*, 2025, **36**(7), 425.
- J. Kim, K. S. Kim and C. W. Myung, Efficient electron extraction of SnO<sub>2</sub> electron transport layer for lead halide perovskite solar cell, *npj Comput. Mater.*, 2020, **6**(1), 100.
- L. Huang, X. Sun, C. Li, J. Xu, R. Xu, Y. Du, J. Ni, H. Cai, J. Li, Z. Hu and J. Zhang, UV-Sintered Low-Temperature Solution-Processed SnO<sub>2</sub> as Robust Electron Transport Layer for Efficient Planar Heterojunction Perovskite Solar Cells, *ACS Appl. Mater. Interfaces*, 2017, **9**(26), 21909–21920.
- Z. Molenda, S. Chambon, D. M. Bassani and L. Hirsch, Electronic Doping in Perovskite Solar Cells, *Adv. Electron. Mater.*, 2024, **10**(10), 2400090.



- 20 J. Jeong, H.-B. Kim, Y. J. Yoon, N. G. An, S. Song, J. W. Kim, M. Kim, H. Jang, D. S. Kim, G.-H. Kim and J. Y. Kim, The introduction of a perovskite seed layer for high performance perovskite solar cells, *J. Mater. Chem. A*, 2018, **6**(41), 20138–20144.
- 21 X. Meng, J. Deng, Q. Sun, B. Zong, Z. Zhang, B. Shen, B. Kang, S. R. P. Silva and L. Wang, High-efficiency planar heterojunction perovskite solar cell produced by using 4-morpholine ethane sulfonic acid sodium salt doped SnO<sub>2</sub>, *J. Colloid Interface Sci.*, 2022, **609**, 547–556.
- 22 P. Wang, B. Chen, R. Li, S. Wang, N. Ren, Y. Li, S. Mazumdar, B. Shi, Y. Zhao and X. Zhang, Cobalt Chloride Hexahydrate Assisted in Reducing Energy Loss in Perovskite Solar Cells with Record Open-Circuit Voltage of 1.20 V, *ACS Energy Lett.*, 2021, **6**(6), 2121–2128.
- 23 T. Bu, J. Li, F. Zheng, W. Chen, X. Wen, Z. Ku, Y. Peng, J. Zhong, Y.-B. Cheng and F. Huang, Universal passivation strategy to slot-die printed SnO<sub>2</sub> for hysteresis-free efficient flexible perovskite solar module, *Nat. Commun.*, 2018, **9**, 4609.
- 24 Z. Yang, Y. Deng, X. Zhang, S. Wang, H. Chen, S. Yang, J. Khurgin, N. X. Fang, X. Zhang and R. Ma, High-Performance Single-Crystalline Perovskite Thin-Film Photodetector, *Adv. Mater.*, 2018, **30**(8), 1704333.
- 25 X. Guo, J. Du, Z. Lin, J. Su, L. Feng, J. Zhang, Y. Hao and J. Chang, Enhanced efficiency and stability of planar perovskite solar cells using SnO<sub>2</sub>:InCl<sub>3</sub> electron transport layer through synergetic doping and passivation approaches, *Chem. Eng. J.*, 2021, **407**, 127997.
- 26 Y. Zhao, L. Gao, Q. Wang, Q. Zhang, X. Yang, J. Zhu, H. Huang, J. Duan and Q. Tang, Reinforced SnO<sub>2</sub> tensile-strength and “buffer-spring” interfaces for efficient inorganic perovskite solar cells, *Carbon Energy*, 2024, **6**(6), e468.
- 27 Q. Feng and G. Nan, How Do A-Site Cations Regulate Trap States at Defective Surfaces of Lead Iodide Perovskites?, *J. Phys. Chem. Lett.*, 2022, **13**(21), 4831–4839.
- 28 Y. Rui, T. Li, B. Li, Y. Wang and P. Mueller-Buschbaum, Two-dimensional SnS<sub>2</sub> nanosheets as electron transport and interfacial layers enable efficient perovskite solar cells, *J. Mater. Chem. C*, 2022, **10**(34), 12392–12401.
- 29 J. Sun, Y. Gu, Y. Lu, J. Hu, T. Chen, C. Zhu and P. Luo, Synergistic strategy of rubidium chloride regulated SnO<sub>2</sub> and 4-butyl-benzylammonium iodide passivated MAxFA1-xPbI3 for efficient mixed-cation perovskite solar cells, *Chem. Eng. J.*, 2023, **468**, 143722.
- 30 L. Xiong, Y. Guo, J. Wen, H. Liu, G. Yang, P. Qin and G. Fang, Review on the Application of SnO<sub>2</sub> in Perovskite Solar Cells, *Adv. Funct. Mater.*, 2018, **28**(35), 1802757.
- 31 S. Das, S. Senapati, G. K. Pradhan, S. Varadharajanperumal and R. Naik, A Facile Microwave-Assisted Nanoflower-to-Nanosphere Morphology Tuning of CuSe1-xTe1+x for Optoelectronic and Dielectric Applications, *ACS Appl. Nano Mater.*, 2023, **6**(7), 5298–5312.
- 32 S. Giri, P. C. Kumar, S. Supriya, D. Alagarasan and R. Naik, Enhanced photodetectivity and responsivity in In10Se70Te15Bi5 film by time-dependent laser irradiation for photodetector applications, *RSC Adv.*, 2025, **15**(55), 46821–46837.
- 33 J. Liu, S. Li, S. Liu, Y. Chu, T. Ye, C. Qiu, Z. Qiu, X. Wang, Y. Wang, Y. Su, Y. Hu, Y. Rong, A. Mei and H. Han, Oxygen Vacancy Management for High-Temperature Mesoporous SnO<sub>2</sub> Electron Transport Layers in Printable Perovskite Solar Cells, *Angew. Chem., Int. Ed.*, 2022, **61**(26), e202202012.
- 34 Y. Ai, W. Liu, C. Shou, J. Yan, N. Li, Z. Yang, W. Song, B. Yan, J. Sheng and J. Ye, SnO<sub>2</sub> surface defects tuned by (NH<sub>4</sub>)<sub>2</sub>S for high-efficiency perovskite solar cells, *Sol. Energy*, 2019, **194**, 541–547.
- 35 X. Tao, H. Chen, Y. Zhou, Q. Peng and Y. Ouyang, The formation energy and interaction energy of point defects in ZrC, *J. Nucl. Mater.*, 2021, **557**, 153235.
- 36 Z. Wang, M. A. Kamarudin, N. C. Huey, F. Yang, M. Pandey, G. Kapil, T. Ma and S. Hayase, Interfacial Sulfur Functionalization Anchoring SnO<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> for Enhanced Stability and Trap Passivation in Perovskite Solar Cells, *Chemosuschem*, 2018, **11**(22), 3941–3948.
- 37 S. B. Hong, S. Kim and H. W. Choi, Improved Performance of Perovskite Deep-Ultraviolet Photodetector Using FAPb(I/Br)<sub>3</sub> as Light Absorption Layer, *Coatings*, 2023, **13**(2), 341.
- 38 D. J. Shin, S. Kim and H. W. Choi, Effect of Methylammonium Iodide (MAI) on MAPbI<sub>3</sub>-Based Perovskite UV-C Photodetectors, *Appl. Sci.*, 2024, **14**(14), 6223.
- 39 W. Qu, S. Weng, L. Zhang, M. Sun, B. Liu, W. Du and Y. Zhang, Self-powered ultraviolet-visible-near infrared perovskite/silicon hybrid photodetectors based on a novel Si/SnO<sub>2</sub>/MAPbI<sub>3</sub>/MoO<sub>3</sub> heterostructure, *Appl. Phys. Express*, 2020, **13**(12), 121001.
- 40 W. Song, J. Lv, J. Li, X. Huang, H. Duan, H. Qin, S. Ma, J. Wei, X. He and Z. Li, Picowatt-Sensitive and Air-Stable Heterojunction UV Photodetectors Enabled by Large-Grained CsCu<sub>2</sub>I<sub>3</sub> Film via Microgap Thermal Sublimation, *ACS Photonics*, 2025, **12**(8), 4478–4488.
- 41 Y. Peng, D. Jiang, M. Zhao, Y. Duan, H. Wei, H. Li, Q. Liang and S. Wang, High-performance UV-visible photodetectors based on ZnO/perovskite heterostructures, *J. Alloys Compd.*, 2023, **965**, 171372.
- 42 H. Zhou, J. Mei, M. Xue, Z. Song and H. Wang, High-Stability, Self-Powered Perovskite Photodetector Based on a CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/GaN Heterojunction with C<sub>60</sub> as an Electron Transport Layer, *J. Phys. Chem. C*, 2017, **121**(39), 21541–21545.
- 43 Y. Yuan, H. Tao, H. Wang, J. Liu, Y. Zhang, Q. Fu, H. Zhao, T. Di, H. Long and S. Yao, The effect of UVO treatment on TiO<sub>2</sub>-MAPbI<sub>3</sub> heterostructure photodetector prepared in air atmosphere, *Mater. Sci. Semicond. Process.*, 2024, **172**, 108079.
- 44 T. Li, H. Wu, Y. Hao, F. Ma, P. Zhu, Z. Li, F. Li, J. Yu, M. Liu, C. Lei and T. Liang, High-Performance Broadband



- Photodetectors Combining Perovskite and Organic Bulk Heterojunction Bifunctional Layers, *Crystals*, 2024, **14**(10), 868.
- 45 X. Xu, Z. Liu, W. Chen, Y. Chen, W. He and Y. Peng, Heteropoly Blue Modified SnO<sub>2</sub> for Highly Efficient Perovskite-Based Photodetectors, *ACS Appl. Energy Mater.*, 2025, **8**(9), 6112–6120.
- 46 S. Fang and Y. H. Hu, Thermo-photo catalysis: a whole greater than the sum of its parts, *Chem. Soc. Rev.*, 2022, **51**(9), 3609–3647.

