

Realizing High-Detectivity Near-Infrared Photodetectors in Tin–Lead Perovskites by Double-Sided Surface-Preferred Distribution of Multifunctional Tin Thiocyanate Additive

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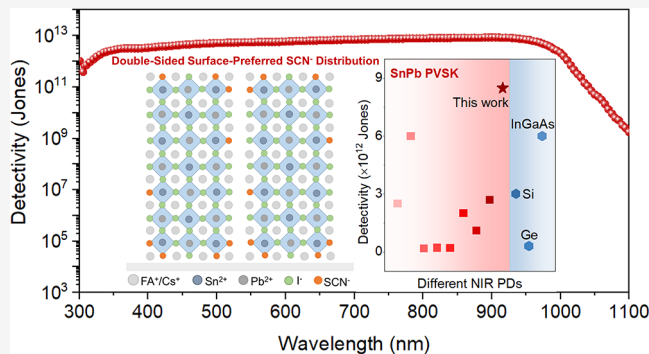


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Supporting Information

ABSTRACT: Tin–lead perovskite photodetectors are attractive alternatives to silicon counterparts for near-infrared photo-detection, due to their outstanding optoelectronic properties, solution processability, and flexible compatibility. However, uncontrollable crystallization and easy oxidation problems of tin-containing perovskites severely hinder advances in their performance. Herein, we develop a high-detectivity near-infrared photodetector using a tailored tin–lead perovskite structure. Notably, we employ tin thiocyanate to form a double-sided surface-preferred distribution in tin–lead perovskites, in which the majority is located at bottom and top surfaces, and the tiny minority positioned inside the films. The tailored perovskite structure with the unique additive distribution significantly improves the film morphology and antioxidation ability. Finally, self-powered tin–lead perovskite photodetectors achieve a peak responsivity of 0.57 A W^{-1} , a detectivity of $8.48 \times 10^{12} \text{ Jones}$ at 910 nm, and a large linear dynamic range of 213 dB, accompanied by an outstanding lifetime of 2300 h. This work opens up a new avenue to developing high-performance near-infrared photodetectors.



Near-infrared photodetectors (NIR PDs) with a spectral response of 780–1100 nm and up to 1800 nm are highly desirable in a variety of applications of imaging sensing, environmental monitoring, day/night surveillance, medical imaging, machine vision, and biometric identification.^{1–4} Most current commercial NIR PDs are fabricated by inorganic semiconductor materials such as silicon and III–V compounds, which demand high temperature, vacuum, and complicated procedures.^{3,5} Solution-processed low-temperature hybrid organic–inorganic perovskite PDs have emerged as attractive alternatives for next-generation photodetection on account of the low cost, easy fabrication processes, and excellent optoelectronic properties of the perovskites (i.e., large absorption coefficient, tunable band gap, high carrier mobility, and long carrier diffusion length).^{6–8} Typical lead perovskite based PDs have been widely researched and achieved impressive performances.^{7,9–12} However, the spectral response of lead perovskite PDs is mainly limited to the UV–vis region, which is determined by the relatively large band gap (around 1.55 eV) of lead perovskites. To expand the spectral range to longer wavelengths, some narrow-band-gap

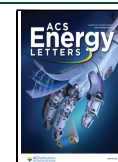
polymers or quantum dots have been employed to integrate with lead perovskites, which effectively helps achieve the widened response but is mostly accompanied by a relatively low efficiency and low measured noise-determined detectivity (around 10^{11} Jones) in the NIR region.^{4,13,14}

Alternatively, partially incorporating tin into lead perovskites has been demonstrated to be an effective method to decrease the perovskite band gap from 1.55 eV to the lowest value of 1.17 eV for tin–lead mixed perovskites, suggesting their great potential as active semiconductor materials for NIR PDs.¹⁵ Nevertheless, the poor film quality and instability of tin–lead perovskites hinder their practical applications. Specifically, the reaction activity of SnI_2 with organic cations is stronger than

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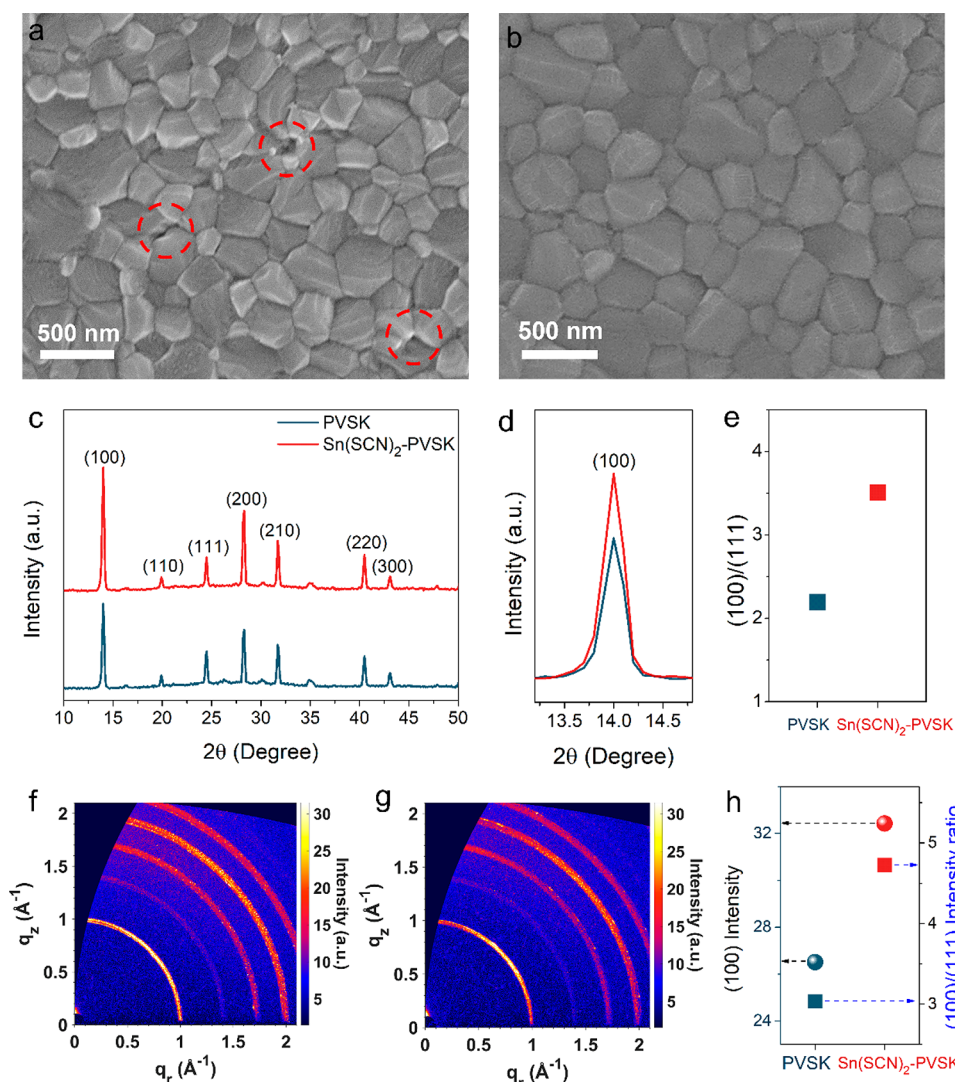


Figure 1. SEM images of (a) pure tin-lead perovskite and (b) $\text{Sn}(\text{SCN})_2$ -perovskite films. Cracks and gaps in the pure tin-lead perovskite film are highlighted by red circles. (c) XRD patterns from 10 to 50°, (d) enlarged XRD patterns from 13.2 to 14.8°, and (e) the intensity ratio of (100)/(111) of pure tin-lead perovskite films and $\text{Sn}(\text{SCN})_2$ -perovskite films, GIWAXS patterns of (f) pure perovskite and (g) $\text{Sn}(\text{SCN})_2$ -perovskite films. (h) GIWAXS intensity of the (100) plane and GIWAXS intensity ratio of (100)/(111) planes.

that of PbI_2 , which leads to a overly fast crystallization process so that a rough surface, pinholes/cracks, and partial coverage have usually been observed in tin-containing perovskite films.^{16–18} Such poor-quality films would introduce an undesirable leakage current and many defects as nonradiative carrier combination centers, potentially resulting in an increase in dark current and a decrease in photocurrent, which would increase the noise current and decrease responsivity and thus reduce detectivity. Promising approaches, such as precursor engineering by DMSO solvent,¹⁹ adjustment of the tin content,²⁰ and solvent-/vacuum-assisted methods,^{21,22} have been studied to improve the crystallization of tin-lead perovskite films. Moreover, the easy oxidation property of divalent tin tends to trigger the instability of tin-lead perovskites. This would induce undesirable traps that detrimentally influence the performance of tin-lead perovskite based PDs and simultaneously reduce the device long-term stability. To suppress the oxidation in pure tin and tin-lead perovskite systems, many antioxidant agents have been adopted to reduce the generation of Sn^{4+} vacancies, including SnF_2 ,²³ an SnF_2 -pyrazine complex,²⁴ tin powder,²⁵ $\text{Sn}(0)$

nanoparticles,²⁶ maltol,²⁷ formamidine sulfinic acid,²⁸ caffeic acid,²⁹ and 4-hydrazinobenzoic acid.³⁰ Overall, due to the above challenges of tin-containing perovskites causing unbalanced crystallization and an oxidation tendency, the achievement of higher detectivity in tin-lead perovskite PDs is severely hindered, which is very important for detecting weak light signals. Consequently, new strategies that simultaneously address these two problems are urgently in demand.

Thiocyanate salts are considered as kinds of effective additives to control the crystallization process and retard the oxidation by the strong interaction between SCN^- and metal cations.³¹ Currently, although some thiocyanate additives such as methylammonium thiocyanate (MASCN)³² and guanidinium thiocyanate (GuaSCN)³³ have been studied, the research on these kinds of additives in the tin-lead perovskite system is still limited. Therefore, in this work, we first employ a tin thiocyanate ($\text{Sn}(\text{SCN})_2$) additive to simultaneously tune crystallization and suppress oxidation of tin-lead perovskite films to develop high-detectivity (approaching 10^{13} Jones) NIR PDs. Interestingly, the $\text{Sn}(\text{SCN})_2$ additive tends to form a unique double-sided surface-preferred distribution within the

perovskite film, the majority being located at the bottom and top surfaces, and the tiny minority being positioned inside the films. The tailored tin-lead perovskite structure with the unique additive distribution significantly contributes to the improvements in morphology and antioxidation ability. Consequently, our self-powered tin-lead perovskite NIR PDs achieve a significantly reduced dark current of $9.85 \times 10^{-8} \text{ A cm}^{-2}$ at -0.4 V , a peak responsivity of 0.57 A W^{-1} , a highest detectivity of $8.48 \times 10^{12} \text{ Jones}$ at 910 nm wavelength, and a large linear dynamic range (LDR) of 213 dB . This work opens up a new avenue to develop high-performance near-infrared photodetectors.

The $\text{Sn}(\text{SCN})_2$ additive was synthesized by a modified method following a previous report.³⁴ The X-ray diffraction (XRD) pattern and energy-dispersive X-ray spectroscopy (EDS) mapping were obtained to characterize the additive material. As shown in Figures S1 and S2 in the Supporting Information, $\text{Sn}(\text{SCN})_2$ was obtained as white needles, and the elements Sn, S, and N were uniformly distributed in the material. Moreover, the XRD peaks of $\text{Sn}(\text{SCN})_2$ located at 16.7° , 17.9° , 19.3° , 21.5° , 23.9° , 28.8° , and 30.6° are in good agreement with previous reports.^{35–37}

The architecture of tin-lead perovskite NIR PDs was designed as indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)/ $\text{FA}_{0.85}\text{Cs}_{0.15}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ /phenyl- C_{61} -butyric acid methyl ester (PCBM)/zirconium acetylacetonate (ZrAcac)/silver (Ag). Perovskite films were prepared by a one-step solution-processed deposition method without or with the introduction of $\text{Sn}(\text{SCN})_2$ additive in the precursor solution. We studied the influence of different $\text{Sn}(\text{SCN})_2$ additive concentrations on the device performance, as shown in Figure S3 in the Supporting Information. Our results show that the introduction of the $\text{Sn}(\text{SCN})_2$ additive can effectively help devices to significantly reduce dark current density and simultaneously increase photocurrent density, which achieve a higher on/off ratio (photocurrent density to dark current density). The optimal concentration of $\text{Sn}(\text{SCN})_2$ additive was evaluated to be 4% (the percentage refers to the molar ratio of $\text{Sn}(\text{SCN})_2$ to metal iodides). The underlying mechanism of the improved performance will be investigated and revealed below in detail in terms of perovskite film morphology and crystallization, additive distributions and roles in the films, antioxidation, defect passivation, and carrier dynamics. In a later discussion, we will use a tin-lead perovskite with optimal 4% $\text{Sn}(\text{SCN})_2$ additive (termed “ $\text{Sn}(\text{SCN})_2$ -perovskite”) for a detailed study.

MORPHOLOGY AND STRUCTURAL CHARACTERIZATIONS

To investigate the effect of $\text{Sn}(\text{SCN})_2$ additive on the morphology of tin-lead perovskite films, a scanning electron microscope (SEM) and atomic force microscope (AFM) were employed. As shown in Figure 1a, the pure perovskite film contains many small grains and cracks around grain boundaries, which would create more opportunities for the formation of defects and thus lead to charge carrier recombination and detrimental current leakage. Meanwhile, the film presents a rough surface with a root-mean-square (rms) roughness of 31.1 nm (Figure S4a in the Supporting Information). Surprisingly, the $\text{Sn}(\text{SCN})_2$ -perovskite film shows a smooth pinhole- and crack-free morphology with a lower rms roughness of 23.1 nm (Figure 1b and Figure S4c in the Supporting Information). Importantly, the grains become

compact and dense, and show relatively increased grain sizes (Figure S5 in the Supporting Information), which are beneficial for the carrier transport that facilitates efficient photodetection. Consequently, the $\text{Sn}(\text{SCN})_2$ additive could effectively tune the crystallization processes of tin-lead perovskite films and thus contribute to the significantly improved film morphology.

Figure 1c compares XRD patterns of pure tin-lead perovskite films and $\text{Sn}(\text{SCN})_2$ -perovskite films. Peaks of (100), (110), (111), (200), (210), (220), and (300) planes are observed for tin-lead perovskites with a pseudocubic crystal structure. The $\text{Sn}(\text{SCN})_2$ -perovskite film shows no shifts of perovskite peaks. Moreover, UV–vis absorption spectra (Figure S6 in the Supporting Information) show that the addition of the optimal $\text{Sn}(\text{SCN})_2$ additive does not change the band gap of tin-lead perovskites. Furthermore, no new XRD peaks or phases from the $\text{Sn}(\text{SCN})_2$ additive (Figure S1 in the Supporting Information) are detected in the $\text{Sn}(\text{SCN})_2$ -perovskite film, suggesting that the presence of $\text{Sn}(\text{SCN})_2$ amount, if any, is below the XRD detection limit. Notably, when the concentration of the $\text{Sn}(\text{SCN})_2$ additive increases to 8%, the slight shifts at the (111), (220), and (300) planes (Figure S7 in the Supporting Information) confirm the presence of SCN^- in the perovskite lattice. A later discussion will show that the presence of the characteristic SCN^- peak (Figure S8 in the Supporting Information) and S signals (Figure S9 in the Supporting Information) were observed by Fourier-transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS), respectively. In addition, the distribution of SCN^- was also observed throughout the whole $\text{Sn}(\text{SCN})_2$ -perovskite film from a time-of-flight secondary-ion mass spectrometry (ToF-SIMS) measurement, which will be discussed in details in the next section. Hence, it could be deduced that no peak shifts in the $\text{Sn}(\text{SCN})_2$ -perovskite film (i.e., the optimal 4% additive) might result from undetectable weak signals due to the partial I^- replacement by the SCN^- with a similar radius ($r_{\text{I}} = 0.22 \text{ nm}$ and $r_{\text{SCN}} = 0.215\text{--}0.22 \text{ nm}$)³⁸ and/or the additive location at grain boundaries.

Interestingly, as shown in Figure 1d, compared to the pure tin-lead perovskite film, the $\text{Sn}(\text{SCN})_2$ -perovskite film has an increased diffraction intensity of the (100) plane that indicates the improved crystallinity, and a reduced value of full width at half-maximum that indicates an increased crystal size, which is consistent with the observed grain size (Figure 1a,b). Furthermore, as shown in Figure 1e, the $\text{Sn}(\text{SCN})_2$ -perovskite film achieves a significantly enhanced plane intensity ratio of (100)/(111) of over 1.5-fold with respect to the pure tin-lead perovskite film, suggesting the strengthened preferred orientation of the (100) plane. Consequently, the introduction of the $\text{Sn}(\text{SCN})_2$ additive in tin-lead perovskite films can effectively improve the crystallinity and phase purity and strengthen the preferred orientation, which would be beneficial for efficient PDs. We used grazing incidence wide-angle X-ray scattering (GIWAXS) to further investigate the crystalline features of tin-lead perovskite films. As shown in Figure 1f,g, the rings of GIWAXS patterns centered around at $q = 1.0, 1.4, 1.7$, and $2.0 \text{ \AA}^{-1}$, where q is the scattering vector, correspond to the diffraction patterns of (100), (110), (111), and (200) planes of perovskite films, respectively. In order to clearly compare the difference between the pure perovskite and the $\text{Sn}(\text{SCN})_2$ -perovskite films, we obtained the intensity data of different diffraction planes from the intensity profile of GIWAXS patterns. As shown in Figure 1h, compared with

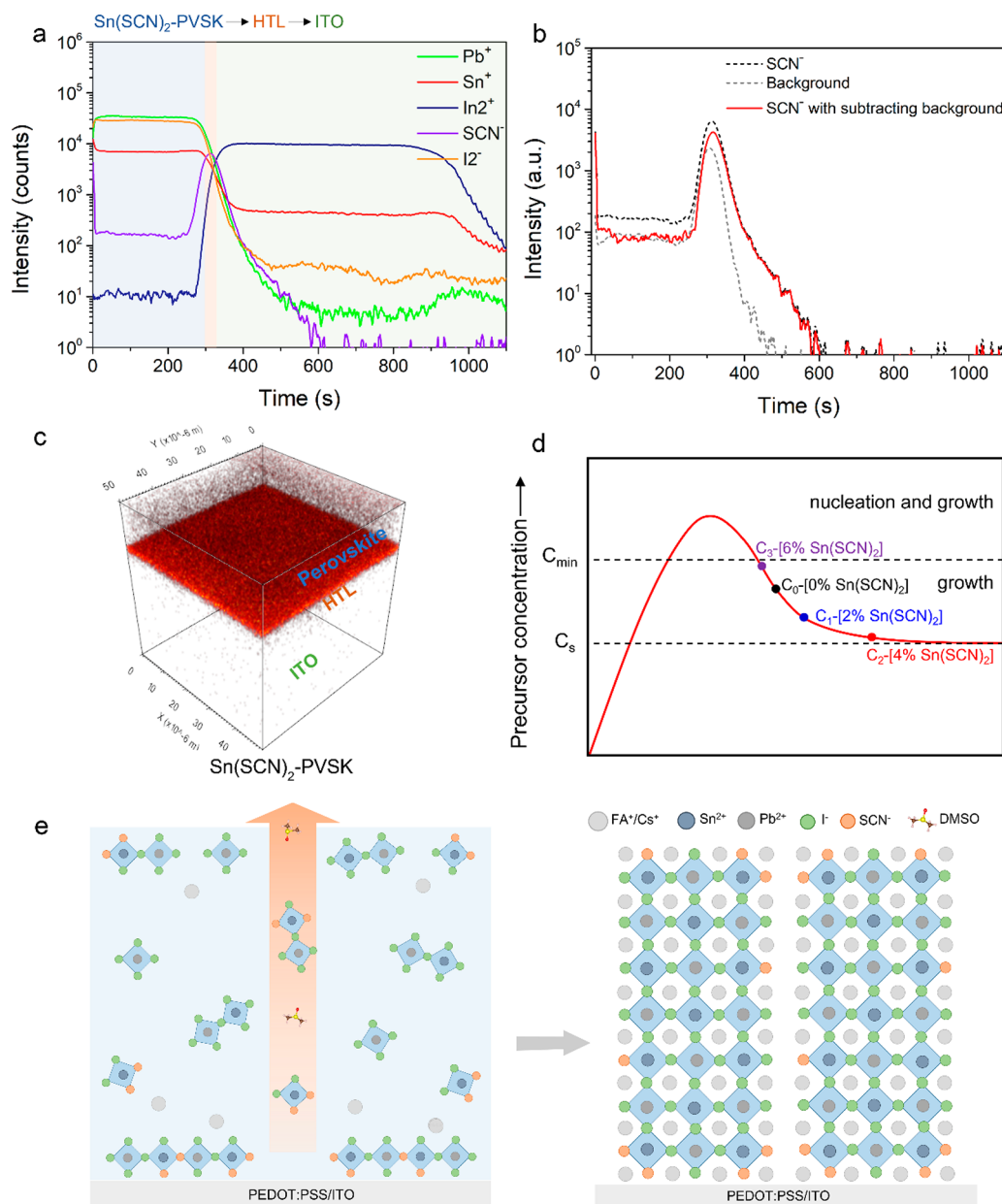


Figure 2. (a) TOF-SIMS depth profiles of $\text{Sn}(\text{SCN})_2$ -perovskite samples. (b) ToF-SIMS depth profiles of SCN^- signals. The SCN^- signal of the pristine sample is denoted “background”, and the signal of $\text{Sn}(\text{SCN})_2$ -perovskite sample is denoted “ SCN^- ”. The SCN^- signal of the $\text{Sn}(\text{SCN})_2$ -perovskite sample with subtraction of the background is shown as a red line. (c) 3D maps of SCN^- ion within the sample of $\text{Sn}(\text{SCN})_2$ -perovskite/HTL/ITO. (d) LaMer-mechanism-based diagram for the top surface crystallization of tin-lead perovskite precursor films with different $\text{Sn}(\text{SCN})_2$ additive concentrations. C_0 , C_1 , C_2 , and C_3 refer to the precursor concentrations of perovskite films with 0%, 2%, 4%, and 6% $\text{Sn}(\text{SCN})_2$ additive, respectively. (e) Schematic diagram of the crystallization mechanism of $\text{Sn}(\text{SCN})_2$ -perovskite.

pure tin-lead perovskites, the $\text{Sn}(\text{SCN})_2$ -perovskite film shows a higher intensity of the (100) plane and also an enhanced (100)/(111) intensity ratio, which indicate the increased crystallinity and preferred growth orientation of the (100) plane by the introduction of $\text{Sn}(\text{SCN})_2$ additive into tin-lead perovskite films.

■ UNIQUE DOUBLE-SIDED SURFACE-PREFERRED ADDITIVE DISTRIBUTION IN TIN-LEAD PEROVSKITE FILMS

To explore the presence of the $\text{Sn}(\text{SCN})_2$ additive in the tin-lead perovskite film, FTIR was employed, as shown in Figure S8 in the Supporting Information. The $\text{Sn}(\text{SCN})_2$ -perovskite

film shows a clear FTIR peak around a wavenumber of 2055 cm^{-1} , which belongs to the C–N stretching of an SCN ion. Notably, the C–N stretching peak in the $\text{Sn}(\text{SCN})_2$ -perovskite film shows a shift from 2070 cm^{-1} in $\text{Sn}(\text{SCN})_2$, suggesting a bond between the additive and tin-lead perovskites (Figure S8 in the Supporting Information), which might passivate uncoordinated metal cations and contribute to $\text{Sn}(\text{SCN})_2$ -containing heterogeneous nuclei (discussed below). Meanwhile, an S 2p signal can be observed in the $\text{Sn}(\text{SCN})_2$ -perovskite film from XPS spectra (Figure S9 in the Supporting Information). By calculating the integral area under S 2p and I 3d peaks, a small S/I ratio of around 0.47% is obtained from the $\text{Sn}(\text{SCN})_2$ -perovskite film. Furthermore, an EDS measurement shows the presence of S element in the film with a similar

S/I ratio of 0.49% (Figure S10 in the Supporting Information). Hence, the small ratio of S element offers direct evidence for the presence of the $\text{Sn}(\text{SCN})_2$ additive in the $\text{Sn}(\text{SCN})_2$ -perovskite film.

We also did ToF-SIMS measurements to investigate the chemical distribution of $\text{Sn}(\text{SCN})_2$ additive within the tin-lead perovskite film. As illustrated in Figure 2a–c and Figure S11 in the Supporting Information, depth profiles and corresponding visualized 3D maps demonstrate the tracking of SCN^- signals throughout the pure tin-lead perovskite and $\text{Sn}(\text{SCN})_2$ -perovskite samples. Clearly, compared with the pure perovskite sample (Figure S11 in the Supporting Information), the $\text{Sn}(\text{SCN})_2$ -perovskite film shows obviously increased intensity of the SCN^- signals (Figure 2a,b), which indicates the presence of the residual $\text{Sn}(\text{SCN})_2$ additive within the film. The abnormal SCN^- signals for the pure perovskite sample could be regarded as a background signal that possibly results from the influence of the hole transport layer (HTL) of PEDOT:PSS with the polystyrenesulfonate group. A similar phenomenon has also been observed in other research.^{39–41} Notably, by comparing SCN^- signals with subtraction of the background in the depth profile (Figure 2b), we can clearly confirm that SCN^- signals show a preferred concentration gradient distribution within the perovskite film, in which most signals are located at the bottom and top surfaces, and weak signals are positioned inside the film. For a better and more accurate indication of the distribution of the additive within the sample, we take a first-order derivative for the depth profiles of Sn, Pb, In, SCN, and I to clearly show the change rates of these elements, as shown in Figure S12 in the Supporting Information. Sn and SCN elements both show a negative change rate at the top surface of the $\text{Sn}(\text{SCN})_2$ -perovskite film, indicating the top surface-preferred distribution of $\text{Sn}(\text{SCN})_2$ additives. For the bottom region of the perovskite film (i.e., near perovskite/HTL), the SCN^- signal has an increased rate and has the greatest increased rate at the interface of perovskite and HTL, which confirms the increased SCN^- intensity from the film interior to the bottom interface, indicating the bottom-preferred distribution of SCN-containing additives. This characteristic distribution is further verified in $\text{Sn}(\text{SCN})_2$ -perovskite film samples with higher concentrations of additives (Figure S13 in the Supporting Information). These results indicate that the addition of $\text{Sn}(\text{SCN})_2$ additive tends to form a double-sided surface-preferred distribution in the pseudohalide SCN^- incorporated perovskite film.

For the bottom-surface-preferred SCN^- accumulation, we first exclude the bonding between $\text{Sn}(\text{SCN})_2$ and the PEDOT:PSS underlay, since there are no peak shifts in a $\text{Sn}(\text{SCN})_2$ /PEDOT:PSS bilayer with respect to separate $\text{Sn}(\text{SCN})_2$ and PEDOT:PSS layers (Figure S14 in the Supporting Information). Hence, it may be deduced that the double-sided surface-preferred distribution of SCN^- might be governed by crystallization dynamics within the nucleation and growth of perovskite grains. Specifically, for the pure tin-lead perovskite, films experience a crystallization competition between the bottom and the top, as shown in Figure S15a in the Supporting Information. The bottom of precursor films usually surrounded by the relatively low-concentration precursors prefers to employ pre-existing nuclei in the precursor solution and slowly grow to large-size grains. Distinctively, the top of precursor films directly treated by antisolvent washing shows the supersaturated states and prefers

to generate numerous new nuclei that result in the fast growth and thus small-size grains. The expected fast growth at the top surface would be inhibited by residual solvents released from the bulk during the first low-temperature annealing (60 °C). Hence, the new nuclei at the top tend to experience Ostwald ripening where small-sized particles are dissolved and redeposited on the surface of large-size particles, which results in the growth of relatively large-size grains at the top (with respect to with small-size grains in the fast growth) after residual solvents are completely removed. Consequently, it could be anticipated that pre-existing nuclei at the bottom consume most intermediates in pure tin-lead perovskite precursor films and thus grow to larger-size grains; meanwhile, the crystallization at the top is suppressed and thus relatively smaller-size grains are grown (Figure S15a in the Supporting Information).

To better understand the distribution and plausible mechanism of the $\text{Sn}(\text{SCN})_2$ additive in the tin-lead perovskite film, the schematic diagram based on a LaMer mechanism are shown in Figure 2d,e. When the additive is introduced into precursor solutions, $\text{Sn}(\text{SCN})_2$ would contribute to pre-existing nuclei composed of soft complexes of organic components coordinated with inorganic components due to the strong coordination between SCN^- and metal cations (Figure S8 in the Supporting Information).^{32,42} After treatment by an antisolvent, $\text{Sn}(\text{SCN})_2$ -containing pre-existing nuclei would be preferentially located at the PEDOT:PSS substrate, as evidenced by the bottom-surface-preferred additive distribution in Figure 2a–c; meanwhile, small amounts of nuclei exist inside the precursor film and at the top (Figure 2e). During the low-temperature annealing, compared with pure precursor films, the bottom with $\text{Sn}(\text{SCN})_2$ -containing pre-existing heterogeneous nuclei would experience a faster growth and thus release large amounts of residual solvents. The released solvents would largely inhibit the crystallization at the top surface of precursor films until the concentration of $\text{Sn}(\text{SCN})_2$ -containing heterogeneous nuclei exceeds the critical value, resulting in grain growth (as shown in Figure 2d, the additive concentration from 0% to 4% facilitates the growth suppression of top grains, and the higher concentration of 6% increases the grain growth).⁴³ Hence, it is observed (Figure S15a–c in the Supporting Information) that the grain growth at the top is largely suppressed when the concentration of the $\text{Sn}(\text{SCN})_2$ additive is increased from 0 to the optimal 4%, in which grains at the top show greatly reduced sizes and even largely coalesce with grains at the bottom. The gradually improved grain growth from 0% to the optimal 4% is consistent with the increased crystallinity (Figure S16 in the Supporting Information) and the reduced surface roughness (Figure S4 in the Supporting Information). When the additive concentration increases to 6%, the grain growth at the top occurs due to the increased concentration of heterogeneous nuclei by excess additives (Figure 2d). This would result in a growth competition between the bottom and the top and thus form grains at the top (Figure S15d in the Supporting Information). Simultaneously, the released solvents from the bulk along grain boundaries would accompany the mass transport, including $\text{Sn}(\text{SCN})_2$ -containing complexes from the bottom to the top (Figure 2e), contributing to the top-surface-preferred additive distribution evidenced by Figure 2a–c. Hence, the higher additive concentration indicates the higher intensity of SCN^- at the top (Figure 2a and Figure S13 in the Supporting

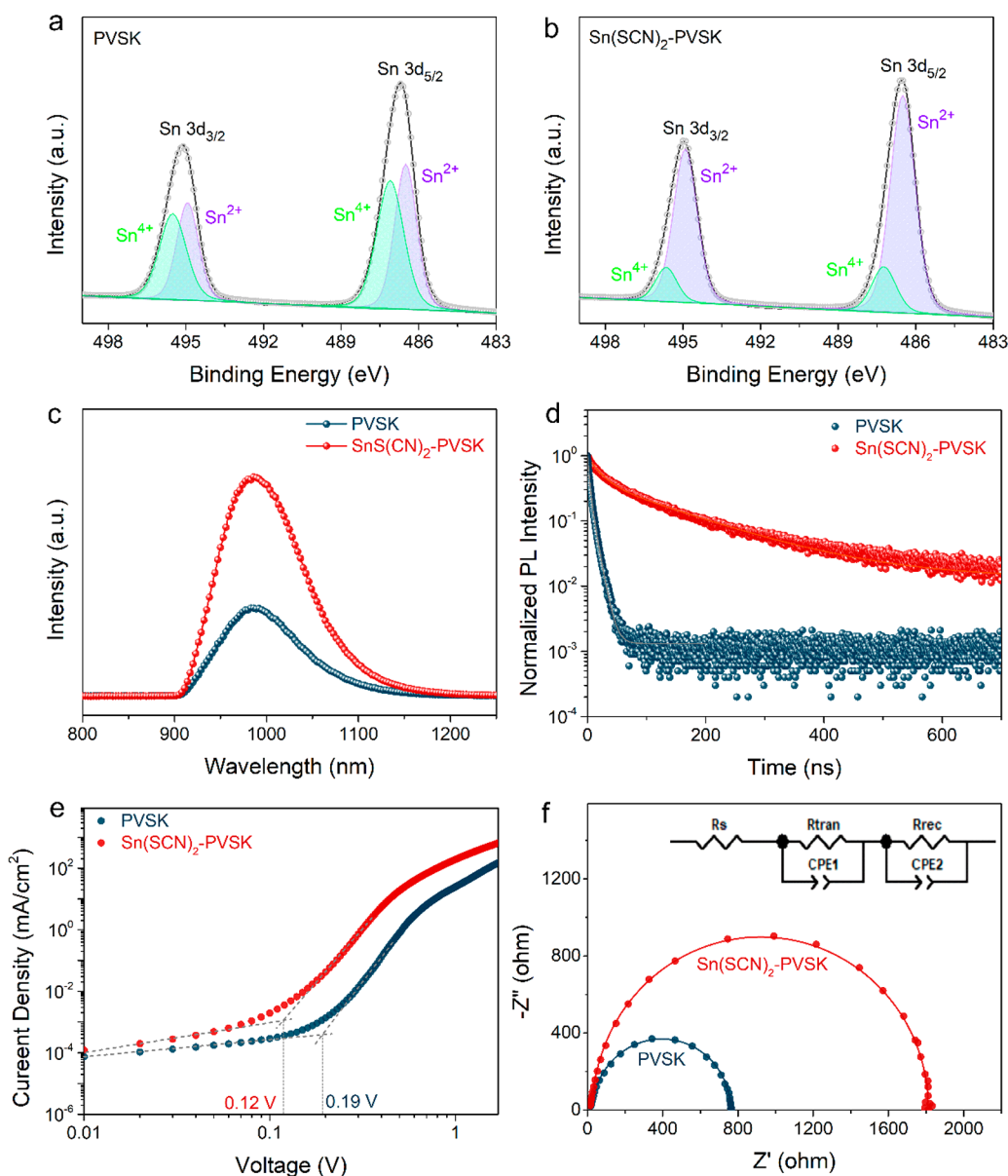


Figure 3. (a, b) Sn 3d XPS spectra and (c, d) PL and TRPL spectra of tin-lead perovskite films. (e) Dark current density–voltage (J – V) curves of hole-only devices. (f) EIS spectra of PDs employing pure tin-lead perovskite and Sn(SCN)₂-perovskite films.

Information) and the increased tendency of additive accumulation at the top grain boundaries (Figure S17 in the Supporting Information), which matches up with the results of increased surface roughness and slightly decreased crystallinity of perovskites with 6% Sn(SCN)₂ additives (Figures S4 and S16 in the Supporting Information). Notably, unlike the case in most reports that the SCN[−] additive from various thiocyanate sources (Pb(SCN)₂, NH₄SCN, MASCN, and GuaSCN) would totally or mostly thermally escape from perovskite films,^{32,33,44,45} our work directly confirms that there is almost no loss of the SCN[−] additive in final Sn(SCN)₂-perovskite films since the S/I ratio in final Sn(SCN)₂-perovskite films obtained from XPS and EDS is about 0.5% (Figures S9 and S10 in the Supporting Information), which is close to the original added source molar ratio (0.7%) of S to I. From the above evidence of the presence and characteristic distribution of SCN signals in the Sn(SCN)₂-perovskite films and the XRD peak shift observed when the concentration of

the Sn(SCN)₂ additive increases to a higher value, it could be deduced that the Sn(SCN)₂-perovskite could keep the 3D structure, and SCN[−] ions tend to replace the iodide anions in the crystal boundaries and preferably passivate the surface dangling sites at the bottom and top regions of the perovskite film. Overall, it is concluded that Sn(SCN)₂ additives tend to form a double-sided surface-preferred distribution ascribed to the crystallization dynamics of tin-lead perovskite grains.

ANTIOXIDATION ABILITY AND CARRIER DYNAMICS

The surface of a tin-lead perovskite film will easily suffer from oxidation and form Sn vacancies and defects; the top-surface-preferred distribution of the Sn(SCN)₂ additive can prevent the oxidation by the strong coordination from SCN[−]. To evaluate the effect of Sn(SCN)₂ additive on suppressing the oxidation of Sn²⁺ to Sn⁴⁺, we used XPS to analyze the chemical state of Sn element. As shown in Figure 3a,b, Sn 3d peaks of

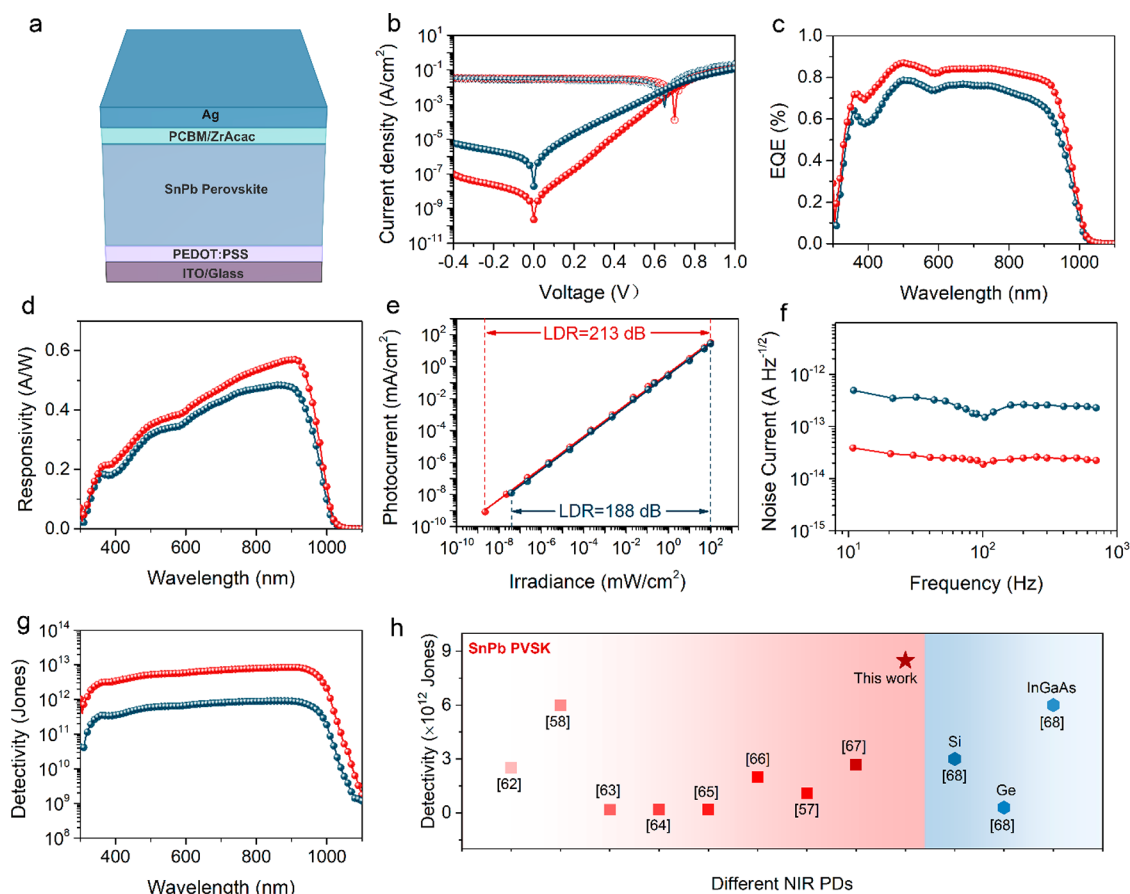


Figure 4. (a) Structure schematic of the tin-lead perovskite PDs. (b) J – V curves under dark condition and AM 1.5G solar illumination, (c) EQE spectra, (d) responsivity, (e) LDR plots of photocurrent density vs incident light intensity, (f) noise currents, and (g) specific detectivity of pure tin-lead perovskite PDs (dark blue) and $\text{Sn}(\text{SCN})_2$ -perovskite PDs (red). (h) Summary of the specific detectivity of NIR PDs.

pure perovskite and $\text{Sn}(\text{SCN})_2$ -perovskite films are deconvoluted into Sn^{2+} and Sn^{4+} peaks. Peaks at 494.9 and 486.5 eV are attributed to the energy levels of $3d^{3/2}$ and $3d^{5/2}$ for Sn^{2+} , respectively, and 495.6 and 487.2 eV are ascribed to the binding energies of Sn^{4+} .^{46,47} After the introduction of $\text{Sn}(\text{SCN})_2$ additive, the $\text{Sn}^{2+}/\text{Sn}^{4+}$ ratio in the $\text{Sn}(\text{SCN})_2$ -perovskite film is significantly increased to 4.92 with respect to the lower value of 0.91 in the pure perovskite film, indicating that the addition of the additive can effectively suppress the level of Sn oxidation. Also, the antioxidation effect of the $\text{Sn}(\text{SCN})_2$ additive can be directly evidenced by the evolution of perovskite precursor solutions under ambient condition, where precursor solutions without the additive quickly tend to turn red due to the presence of Sn^{4+} states (Figure S18 in the Supporting Information). The antioxidation nature of the additive could result from the strong interaction between SCN^- and metal cations that influences the binding energy shift of metal cations (Figure S19 in the Supporting Information). Notably, the unique double-sided surface-preferred additive distribution remarkably improves the antioxidation ability of tin-lead perovskite films. The top additive separates the inner from the outer environment (e.g., moisture and oxygen). Simultaneously, the bottom and interior additive passivates the dangling bonds of metal cations at grain boundaries which thus reduces oxidation channels.⁴⁸ The decreased concentration of Sn^{4+} states could suppress the formation of Sn^{2+} vacancies and defects in Sn-containing

perovskite materials, which could reduce nonradiative recombination and thus increase the photocurrent and suppress the dark current of PDs. Therefore, the antioxidation nature of the additive together with the unique additive distribution greatly suppresses the oxidation of Sn^{2+} in $\text{Sn}(\text{SCN})_2$ -perovskite films, potentially resulting in efficient photodetection.

Steady-state photoluminescence (PL) and time-resolved PL (TRPL) are used to explore the carrier dynamics and defect passivation in pure perovskite and $\text{Sn}(\text{SCN})_2$ -perovskite films, as shown in Figure 3c,d. It is worth noting that the $\text{Sn}(\text{SCN})_2$ -perovskite film presents a stronger PL intensity with an enhancement ratio of about 2.5 compared with that of the pure perovskite film, suggesting the dramatically reduced trap-assisted nonradiative recombination in the $\text{Sn}(\text{SCN})_2$ -perovskite film. Moreover, PL lifetimes were obtained by fitting the TRPL curves according to the biexponential decay equation $I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. The PL decay is composed of fast decay (τ_1) and slow decay (τ_2), which correlate with trap-assisted surface recombination and bulk radiative recombination, respectively. The detailed fitting parameters are given in Table S1 in the Supporting Information. Compared with the pure perovskite film, the fast decay time of the $\text{Sn}(\text{SCN})_2$ -perovskite film shows a 7-fold increase to 20.59 ns, and the slow decay time shows a 16-fold increase to 135.49 ns. The significantly improved fast decay time and slow decay time suggest that the $\text{Sn}(\text{SCN})_2$ additive

could effectively reduce surface and bulk trap densities, which is consistent with the $\text{Sn}(\text{SCN})_2$ distribution in the tin-lead perovskite film (Figure 2). As expected, the average carrier lifetime of the pure perovskite film (6.4 ns) sharply increases to 116.2 ns for the optimized $\text{Sn}(\text{SCN})_2$ -perovskite film.

The $\text{Sn}(\text{SCN})_2$ additive could tune the crystallization and suppress the oxidation of Sn^{2+} states that contribute to the reduced trap densities. Moreover, the $\text{Sn}(\text{SCN})_2$ additive could reduce the loss of iodine, since perovskite films with $\text{Sn}(\text{SCN})_2$ additives achieve higher and consistent I^{2-} intensities (Figure 2a and Figure S13 in the Supporting Information) with respect to the pure perovskite film (Figure S11a in the Supporting Information). The reduced iodine loss would suppress the formation of iodine vacancies and defects that reduce photodetection performance.⁴⁹ To verify the decreased trap density of perovskite films with $\text{Sn}(\text{SCN})_2$ additive, a space-charge-limited-current (SCLC) measurement was conducted in the dark with a device structure of ITO/PEDOT:PSS/perovskites/PTAA/Ag. From Figure 4e, we obtain the trap density (N_t) from the trap-filling limit voltage (V_{TFL}) according to the equation $N_t = (2\epsilon_0\epsilon V_{\text{TFL}})/(qL^2)$, where ϵ_0 , ϵ , q , and L are the vacuum permittivity, the relative dielectric constant of perovskites, the electron charge, and the thickness of the perovskite film, respectively. The $\text{Sn}(\text{SCN})_2$ -perovskite film achieves a trap density of $6.6 \times 10^{14} \text{ cm}^{-3}$, which is much lower than that of the pure perovskite film ($1.1 \times 10^{15} \text{ cm}^{-3}$). This remarkable decrease in trap density in the $\text{Sn}(\text{SCN})_2$ -perovskite film results in an enhanced PL intensity (Figure 3c) and an increased carrier lifetime (Figure 3d), which are beneficial for efficient PDs.

Electrochemical impedance spectroscopy (EIS) was used to quantitatively study the effect of $\text{Sn}(\text{SCN})_2$ additive on charge dynamics. Figure 3f shows the Nyquist plots with an inserted equivalent circuit of tin-lead perovskite PDs. The fitted parameters including three types of resistances (R_s , R_{tr} , and R_{rec}) are given in Table S2 in the Supporting Information. In general, R_s represents the series resistance between electrodes. R_{tr} corresponds to the charge transfer resistance at interfaces of carrier transport layers and perovskite. R_{rec} stands for the recombination resistance for electron and hole recombination within the device.^{50,51} Therefore, the charge transport ability is inverse with the values of R_s and R_{tr} , and the recombination process is limited by the value of R_{rec} . Clearly, $\text{Sn}(\text{SCN})_2$ -perovskite PDs show lower values of R_s and R_{tr} but a higher value of R_{rec} , indicating that the introduction of $\text{Sn}(\text{SCN})_2$ additive facilitates the charge transport and reduces the recombination rate within the device. These improvements contribute to the longer carrier lifetime (Figure 3d) and more efficient carrier transport and extraction, which would result in a higher efficiency and detectivity of tin-lead perovskite NIR PDs (a detailed discussion will be given in the next section).

DEVICE PERFORMANCE

We have studied the influence of $\text{Sn}(\text{SCN})_2$ additive on the performance of NIR PDs (the structure of the device is shown in Figure 4a), including J - V curves in the dark and under light illumination, external quantum efficiency (EQE), responsivity (R), LDR, noise current, and specific detectivity (D^*). As shown in Figure 4b, the dark current density (J_D) of $\text{Sn}(\text{SCN})_2$ -perovskite PDs is significantly suppressed to be over 2 orders of magnitude lower than that of pure perovskite PDs without the additive (termed "reference PDs"), which is reduced from 5.89×10^{-6} to $9.85 \times 10^{-8} \text{ A cm}^{-2}$ at -0.4 V .

The remarkable J_D reduction mainly originates from the eliminated pinholes/cracks, reduced roughness (Figure 1b and Figure S4c in the Supporting Information), and suppressed trap densities (Figure 3e). Meanwhile, with the dense and compact grain distribution, smooth morphology, and enhanced crystallinity, the photocurrent density (J_{ph}) of $\text{Sn}(\text{SCN})_2$ -perovskite PDs increases, implying an efficient carrier transport within the device. Additionally, the $\text{Sn}(\text{SCN})_2$ -perovskite PDs show almost no hysteresis compared with the obvious hysteresis observed in referenced PDs (Figure S20 in the Supporting Information), which is closely related to the significantly reduced defect states (Figure 3). The largely suppressed J_D and enhanced J_{ph} promote the PDs to achieve a high D^* and a large LDR. Figure 4c,d gives the EQE and responsivity spectra, respectively. The EQE spectra of the PDs were measured in the photovoltaic mode, and the responsivity was obtained by $R = \text{EQE} \cdot e/h\nu$, where e is elementary charge, h is Planck's constant, and ν is light frequency. The EQE is enhanced by the $\text{Sn}(\text{SCN})_2$ additive, further confirming the significantly improved carrier transport and photocurrent extraction. Notably, $\text{Sn}(\text{SCN})_2$ -perovskite PDs present a broad response from 300 to 1050 nm and achieve a high flat EQE of around 80% at 450–910 nm and a peak responsivity of 0.57 A/W at 910 nm, which is almost 2 times higher than that of the reported lead perovskite/organic bulk junction PDs^{52–54} and perovskite/quantum dot based PDs.^{55,56}

LDR is defined by a linear range of output photocurrents versus incident light intensities following $\text{LDR} = 20 \times \log(P_{\text{max}}/P_{\text{min}})$ (P_{max} and P_{min} are the upper and lower limits of incident light intensity in the linear range, respectively). As shown in Figure 4e, compared with the reference PDs, P_{min} of $\text{Sn}(\text{SCN})_2$ -perovskite based PDs is at a much lower limit of 2.25 pW/cm², showing the excellent ability of our PDs in detecting weak light signals. This lower limit of LDR is typically determined by the noise current of the device, which is related to thermal noise, shot noise, and flicker noise.^{57,58} Shunt resistance within devices typically contributes to the thermal noise. $\text{Sn}(\text{SCN})_2$ -perovskite PDs have a shunt resistance of 91 G Ω , over 2 orders of magnitude larger than that of a reference device (0.69 G Ω), which leads to largely reduced thermal noise (13.5 fA/Hz^{1/2}). The shot noise of $\text{Sn}(\text{SCN})_2$ -perovskite PDs is also reduced by the substantial decrease of reverse leakage current, which is estimated to be 2.4 fA/Hz^{1/2}. From Figure 4f, our NIR PDs show an almost frequency-independent feature, implying the negligible flicker noise. As a result, the total noise current (i_n) of $\text{Sn}(\text{SCN})_2$ -perovskite PDs is found to be 19 fA/Hz^{1/2}, which is much lower than that of reference PDs and consistent with the calculated noise current of 13.7 fA/Hz^{1/2}. The reduced noise current can be ascribed to the multifunctional features of the $\text{Sn}(\text{SCN})_2$ additive in tin-lead perovskite films, including the compact/pinhole-free/smooth morphology, increased crystallinity, strengthened preferred orientation, and reduced oxidation and trap densities. The low noise current improves the lowest limit of detectable light signals and thus enhances the detectivity. The upper limit of LDR is governed by the lowest carrier mobility of PCBM within the device. As shown in Figure 4e, the reference and $\text{Sn}(\text{SCN})_2$ -perovskite PDs present a similar maximum value of the upper limit. The measured maximum light intensity for $\text{Sn}(\text{SCN})_2$ -perovskite based PDs in our case is 100 mW cm⁻². Consequently, the $\text{Sn}(\text{SCN})_2$ -perovskite PDs achieve a large LDR of 213 dB, which is much larger than those of most NIR PDs based on

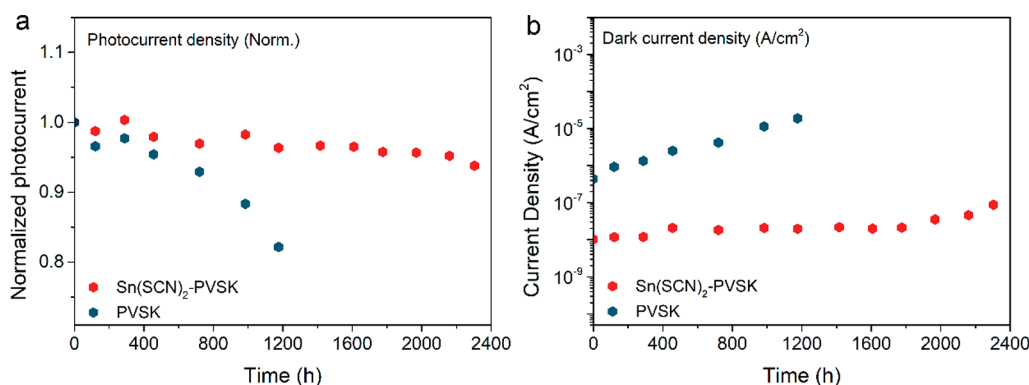


Figure 5. Stability of (a) the normalized photocurrent and (b) the dark current density of unencapsulated NIR perovskite PDs stored under an N₂ atmosphere.

inorganic/perovskite or polymer/perovskite active materials.^{14,59–61}

Specific detectivity D^* is one of the most important parameters for PDs, which is defined by the formulas

$$D^* = (AB)^{1/2} / \text{NEP} \quad (1)$$

$$\text{NEP} = i_n / R \quad (2)$$

where A is the detection area of PDs, B is the bandwidth, and NEP is the noise equivalent power. As shown in Figure S21 in the Supporting Information, Sn(SCN)₂-perovskite PDs present a much lower NEP than that of reference PDs from 300 to 1100 nm and show a lowest value of 3.33×10^{-14} W Hz^{-1/2} in the NIR region. The detectivity spectra as a function of spectral wavelength is shown in Figure 4g. Benefiting from the largely increased responsivity and reduced noise current, the detectivity of Sn(SCN)₂-perovskite PDs is increased by about 1 order of magnitude compared with that of reference PDs, and reaches a largest D^* of 8.48×10^{12} Jones at 910 nm. Notably, to the best of our knowledge, this is the largest peak value of detectivity among tin-lead perovskite based NIR PDs,^{57,58,62–67} and the value is also higher than those of conventional inorganic Si, Ge, and InGaAs NIR PDs,⁶⁸ as shown in Figure 4h and Table S3 in the Supporting Information. We also measured a commercial photodetector of a FDS1010 Si photodiode by the same measurement technology (see details in Experimental Section). The measured noise current and specific detectivity of the FDS1010 Si photodiode are 2.2×10^{-13} A Hz^{-1/2} and 3.0×10^{12} Jones, respectively, which are almost in accordance with the given values from the Thorlab company (as shown in Figure S22 in the Supporting Information).

We measured the transient photocurrent response (TPC) with a 532 nm, 6 ps pulse width laser in an ambient environment to study the ability of PDs recording a high-frequency input optical signal. The response speeds are represented by rise time and fall time, which are defined by the time intervals of stable photocurrents changing between 10% and 90%. As shown in Figure S23 in the Supporting Information, Sn(SCN)₂-perovskite PDs achieve a rise time of 67.5 ns and a fall time of 0.72 μs. Therefore, it can be seen that the response time of the device is indicated by the relatively long fall time, which is dominated by the RC time constant. We calculated the RC time constant ($\text{RC} = RQ/V$), achieving a value of 0.52 μs (Figure S24 in the Supporting Information), which is close to the measured fall time. The discrepancy may

result from other series resistances in the circuit for the device.¹¹ We also measured the transient photocurrent response of Sn(SCN)₂-perovskite PDs as a function of different load resistances, as shown in Figure S25 in the Supporting Information. It can be clearly seen that the photocurrent response time is gradually prolonged with the increase of load resistances, which confirms that the response time of the perovskite PDs is governed by the RC time constant. Moreover, compared with reference PDs (Figure S23 in the Supporting Information), the Sn(SCN)₂-perovskite PDs have a faster fall time, implying that the additive effectively suppresses the detrimental space carrier accumulation induced by defects within the device.

The stability of the unencapsulated Sn(SCN)₂-perovskite PDs was investigated by recording the photocurrent density and dark current density under -100 mV, as shown in Figure 5. The Sn(SCN)₂-perovskite PDs present a stability more superior to that of the reference by storing under an N₂ atmosphere. The photocurrent of Sn(SCN)₂-perovskite PDs was well maintained and finally can retain 94% of the initial value after 2300 h (Figure 5a). Meanwhile, the dark current was conserved at the same order of magnitude, showing a slight increase from the initial 1.04×10^{-8} A cm⁻² to the final 8.80×10^{-8} A cm⁻² after storing 2300 h (Figure 5b). Consequently, with the incorporation of Sn(SCN)₂ additive, the unencapsulated perovskite NIR PDs show very good storage stability.

In summary, we demonstrate high-performance NIR PDs by using a tailored tin-lead perovskite structure. Particularly, a Sn(SCN)₂ additive is introduced to realize a double-sided surface-preferred distribution in the perovskite film. It is distributed mostly at the bottom and top regions, with a tiny amount inside the film. With the unique distribution of the additive, the tailored tin-lead perovskite structure not only shows improved film quality with compact, smooth and pinhole-/crack-free morphologies, reduced roughness, and increased crystallinity but also exhibits enhanced antioxidation, suppressed iodine loss, and defect passivation. Finally, we realize the high-detectivity self-powered tin-lead perovskite NIR PDs with a largely reduced dark current of 9.85×10^{-8} A cm⁻² at -0.4 V, a peak responsivity of 0.57 A/W, a highest detectivity of 8.48×10^{12} Jones at 910 nm, and a large LDR of 213 dB. The unencapsulated PDs also have a very attractive lifetime of 2300 h. Consequently, this research offers a unique architecture tailoring for perovskite photodetectors and also for

other semiconductor devices, which opens up a new avenue for next-generation near-infrared photodetection.

■ EXPERIMENTAL SECTION

Synthesis of Sn(SCN)₂ Additive. A 10 mM amount of SnSO₄ was dissolved in 19 mL of deionized (DI) water with diluted H₂SO₄. A 20 mM amount of NaSCN was dissolved in 2 mL of DI water. Then the NaSCN solution was dropped into the solution of SnSO₄ with stirring. After standing still for several minutes, the mixed solution was kept at 4 °C for 24 h. After washing three times with cold DI water, the product was dried under vacuum for one night. The collected material was stored in the glovebox (O₂ <0.1 ppm, H₂O <0.1 ppm).

Fabrication of Tin–Lead Perovskite Films. The pure perovskite film is formed with a precursor solution including 372.5 mg of SnI₂ (Alfa Aesar, 99.999%), 77.9 mg of CsI (Sigma-Aldrich, 99.999%), 292.3 mg of FAI (GreatCell Solar Limited, 99.99%), 461 mg of PbI₂ (TCI, 99.99%), and 15.6 mg pf SnF₂ (Sigma-Aldrich, 99%) in 1 mL of a mixed solution of DMF (Acros, 99.8%) and DMSO (Acros, 99.7+%). For the perovskite films with additives, certain amounts of Sn(SCN)₂ materials were added to the above precursor solution. After totally dissolving and filtering with a 0.22 μm PTFE filter, the precursor solutions were spun with a spin-coating process of 4000 rpm with a ramp rate of 5000 rpm/s for 30 s, and 300 μL of toluene antisolvent was dripped onto the substrate at the 15th second when stabilizing at the high speed. Finally, films were annealed at 60 and 100 °C for 5 min, respectively.

Device Fabrication. First, ITO glasses were cleaned with detergent, DI water (three times), acetone, and ethanol for 10 min, successively, followed by drying with a stream of nitrogen gas. After treatment by ultraviolet-ozone for 1 h, a PEDOT:PSS (Clevios P VP Al 4083) solution was spin-coated on the substrates at 4000 rpm and was annealed in air at 150 °C for 10 min. Then, samples were transferred into the glovebox with an N₂ atmosphere, and the perovskite films were formed on the PEDOT:PSS-coated ITO/glass substrates. Subsequently, a PCBM/CB solution (20 mg/mL) was spun on perovskite films at 1200 rpm for 35 s, followed by a dynamic spin-coating process of ZrAcac/IPA solution (2 mg/mL) at 3000 rpm. Finally, a 100 nm Ag electrode was thermally deposited under a vacuum of 10^{−6} Torr. The active area of our PDs was 0.08 cm².

Film Characterization. SEM images were measured with LEO 1530FEG scanning electron microscope, the roughness was characterized with an NT-MDT NTEGRA instrument, an XRD test was conducted by using Cu Kα radiation (Rigaku, Smartlab), and GIWAXS was measured by a Xeuss 2.0 SAXS/WAX laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å, incidence angle 0.3°) and a Pilatus 3R 300K detector. TOF-SIMS were characterized with a Physical Electronics 7200 ToF-SIMS spectrometer, XPS spectra were collected with a Physical Electronics 5600 multi-technique system with an Al Kα X-ray source, and PL and TRPL measurements were performed with a PicoQuant FluoTime 300 instrument. UV–vis absorption spectra were obtained with a Shimadzu UV–visible spectrophotometer (UV-2600).

Device Characterization. Current density as a function of voltage was recorded using a Keithley 2400 instrument in dark condition and under simulated AM1.5 sunlight generated by a solar simulator (SS-F5-3A, Enli Technology Co., Ltd.). EIS was carried out with an electrochemical workstation (Zahner, Zennium Pro) under dark condition. EQE measure-

ments were obtained with a home-built system with a 1000 W xenon arc lamp light source setup. A linear dynamic range test was performed under different light intensities of monochromatic light by using Thorlabs metallic-coated neutral density filters. A facility-calibrated (Newport) Si photodetector was used to measure the intensity of monochromatic light. The noise current against different frequencies was recorded with a Stanford Research SR830 DSP lock-in amplifier with a current gain of 10⁸, corresponding to a 13 fA Hz^{−1/2} input current noise of the lock-in system and a measurement bandwidth of 700 Hz. The transient photocurrent response was conducted with a 532 nm, 6 ps pulse width laser (130 μJ pulse^{−1} maximum @400 Hz) and monitored by a 4 GHz Keysight MSO9404A digital oscilloscope.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenerylett.2c02055>.

XRD and EDS of Sn(SCN)₂ materials, on/off ratio, photocurrent, and dark current density of PDs against additive concentrations, AFM of perovskite films, grain-size distributions and absorption spectra of pure perovskite and Sn(SCN)₂-perovskite films, XRD of perovskite films with 0% and 8% Sn(SCN)₂ additives, FTIR of pure perovskite, Sn(SCN)₂-perovskite films, and Sn(SCN)₂, S XPS spectra of pure tin-lead perovskite and Sn(SCN)₂-perovskites and integral area of I and S spectra in Sn(SCN)₂-perovskite films, EDS of Sn(SCN)₂-perovskites, TOF-SIMS depth profiles and 3D map of SCN ions within the sample of pure perovskite and Sn(SCN)₂-perovskites with 6% and 8% additives, first-order derivative for the TOF-SIMS depth profiles, FTIR of Sn(SCN)₂/PEDOT:PSS and separate Sn(SCN)₂ and PEDOT:PSS, cross-sectional SEM, XRD, and SEM of perovskite films with different additive concentrations, evolution of perovskite precursor solutions with or without additive under ambient conditions, Sn and Pb XPS spectra of pure perovskite and Sn(SCN)₂-perovskite films, *J*–*V* curves by forward and reverse scanning and NEP of PDs, parameters of a commercial FDS1010 Si photodiode, TPC of PDs, RC time constant from the photocurrent response of Sn(SCN)₂-perovskite PDs. Transient photocurrent response of PDs as a function of different load resistances, fitted parameters for TRPL, fitted parameters for EIS, and a comparison of the specific detectivity in this work with those of other tin-lead perovskite NIR PDs and conventional inorganic NIR PDs (PDF)

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Notes

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