

Low-Bandgap Methylammonium-Rubidium Cation Sn-Rich Perovskites for Efficient Ultraviolet–Visible–Near Infrared Photodetectors

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Solution-processed and low-temperature Sn-rich perovskites show their low bandgap of about 1.2 eV, enabling potential applications in next-generation cost-effective ultraviolet (UV)–visible (vis)–near infrared (NIR) photodetection. Particularly, the crystallization (crystallinity and orientation) and film (smooth and dense film) properties of Sn-rich perovskites are critical for efficient photodetectors, but are limitedly studied. Here, controllable crystallization for growing high-quality films with the improvements of increased crystallinity and strengthened preferred orientation through a introducing rubidium cation into the methylammonium Sn-Pb perovskite system (65% Sn) is achieved. Fundamentally, the theoretical results show that rubidium incorporation causes lower surface energy of (110) plane, facilitating growth in the dominating plane and suppressing growth of other competing planes. Consequently, the methylammonium-rubidium Sn-Pb perovskite photodetectors simultaneously achieve larger photocurrent and lower noise current. Finally, highly efficient UV–vis–NIR (300–1100 nm) photodetectors with record-high linear dynamic range of 110 and 3 dB cut-off frequency reaching 1 MHz are demonstrated. This work contributes to enriching the cation selection in Sn-Pb perovskite systems and offering a promising candidate for low-cost UV–vis–NIR photodetection.

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1. Introduction

Photodetectors (PDs), spectral response from ultraviolet (UV)–visible (vis)–near infrared (NIR) region, are of great interest due to a variety of scientific and industrial applications, including UV dosimetry and sensing, vis-light sensors, and NIR fluorescent imaging.^[1,2] As an alternative to traditional PDs with high-vacuum and high-temperature fabrication processes, solution-processed and low-temperature materials have emerged as promising candidates for applications in next-generation cost-effective photodetection.^[2] Recently, hybrid organic–inorganic lead perovskite-based PDs have been widely studied and achieved remarkable device performances.^[3,4] However, these PDs cannot sense the light with wavelength beyond 800 nm, limiting broad applications of NIR detection. Polymers and quantum dots have been incorporated to lead perovskite-based PDs and thus widen spectral response

to about 1000 nm.^[5–7] However, these devices have relatively low efficiency at 800–1000 nm. Recently, alloyed Sn-Pb perovskites have been demonstrated to extend the absorption to about 1050 nm, indicating their potential applications in NIR photodetection.^[8–15]

The presence of pinholes, rough surfaces, and low surface coverage in Sn-Pb perovskite films has been reported in early studies.^[8,16] These will lead to severe shorting and fast electron/hole recombination, limiting the device efficiency advances. Recently, several methods, including methylammonium (MA):formamidinium (FA) engineering,^[10,12,17] elevated temperature processing,^[14] lead-assisted two-step method,^[11] and precursor-assisted crystallization,^[15] have been proposed to deposit flat and dense Sn-Pb perovskite films with average Sn content ≤50%. Generally, Sn-Pb perovskites with the Sn content between 60 and 80% reveal the lowest bandgap of ≈1.2 eV.^[8,10,13] However, the investigation of controlling the crystallization (crystallinity and orientation) and film (smooth and dense film) properties of Sn-Pb perovskites (the Sn content > 60%) and their influence on PDs performances still have been rarely reported.^[18]

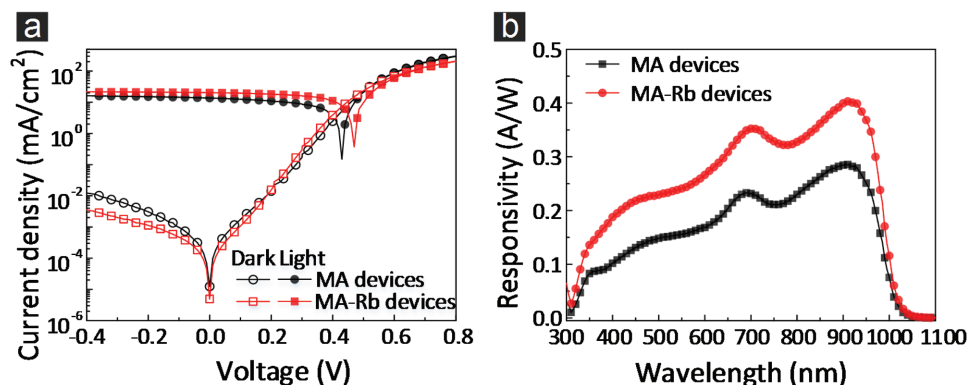


Figure 1. a) Current density against the working bias of MA-based and MA-Rb-based PDs in a dark room and under light illumination, respectively. b) Responsivity of MA-based and MA-Rb-based PDs, respectively.

In this work, we first introduce small-content rubidium cation into MA-based Sn-Pb perovskite system (65% Sn) to achieve controllable crystallization and thus induce growth of dense films with the improvements of increased crystallinity and strengthened preferred orientation. To explain the improvements, we find out that rubidium incorporation not only increases the orbital interaction between Sn/Pb and I atoms but also influences hydrogen bonding between methylammonium and halide frames. Our theoretical results show that the improvements are also due to the lowering of surface energy of (110) plane through the introduction of rubidium. The optimized MA-Rb Sn-Pb perovskite (MA_{0.975}Rb_{0.025}Sn_{0.65}Pb_{0.35}I₃) based PDs achieve UV-vis-NIR broad spectral detection (300–1100 nm) with record-high linear dynamic range (LDR) of 110 and 3 dB bandwidth reaching 1 MHz, offering a promising candidate for low-cost UV-vis-NIR photodetection and enriching the selection of cations in the Sn-Pb perovskite system.^[19]

2. Results and Discussion

2.1. Increased Photocurrent and Reduced Dark Current

Sn-Pb perovskite-based PDs were fabricated with the structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)/Sn-Pb perovskites/PC₆₁BM/zirconium(IV) acetylacetonate (ZrAcac)/Ag. The detailed fabrication procedure can be found in the Experimental Section. To achieve broad spectral detection, the Sn content in MASn_xPb_{1-x}I₃ perovskites ($x = 0.25, 0.50, 0.65, 0.75$) was optimized. As shown in Figure S1 (Supporting Information), it is found that the spectral response of 65%-Sn-based MASn_{0.65}Pb_{0.35}I₃ perovskite PDs red-shifts toward 1100 nm and thus achieves broad UV-vis-NIR photodetection.

High-quality Sn-Pb perovskite films related with smooth and dense film, high crystallinity, and strengthened preferred orientation are vital to realize efficient photodetection. However, related works have been scarcely reported. Interestingly, we first revealed (Figure S2, Supporting Information) that Rb incorporation into MA (MA-Rb) based Sn-Pb perovskites could efficiently increase device on/off ratio (photocurrent to dark

current). We study the effects of Rb concentrations on PD performances as shown in Figure S2 (Supporting Information). We find that the optimized Rb content is 2.5%. The underlying mechanism correlated with perovskite crystallinity and orientation will be discussed below in details.

Specifically, it is clearly seen from current density–voltage curves shown in Figure 1a that MA-Rb-based PDs simultaneously presented reduced dark current and improved photocurrent density. Suppressing dark current and enhancing photocurrent of PDs are of importance for achieving the large LDR and high specific detectivity, enabling PDs to sense the low-level light intensity.^[3] Meanwhile, as shown in Figure S3 (Supporting Information), negligible dark current and photocurrent hysteresis were observed in our PDs, which might be ascribed to reduced surface trap density by the electron-extracting layer PC₆₁BM.^[20] This negligible hysteresis can effectively eliminate the possibility of overestimating/underestimating device performances that happened in hybrid perovskite optoelectronic devices. Responsivity shown in Figure 1b and external quantum efficiency (EQE) shown in Figure S4 (Supporting Information) further confirmed that MA-Rb-based PDs achieved increased photocurrent density. More importantly, MA-Rb-based PDs showed broad spectral response ranging from 300 to about 1100 nm, and achieved the peak responsivity of about 0.4 A W⁻¹ at 910 nm, which is at least two times larger than that of previously reported broad spectral lead perovskite/polymers or lead perovskite/quantum dots based PDs, and larger than that of quantum dots p-n heterojunction based PDs.^[5–7,21,22]

2.2. Influence of MA-Rb Cation on Crystallization of Sn-Pb Perovskites

Scanning electron microscope (SEM) and atomic force microscopy (AFM) were employed to characterize the top-view morphology of MA and MA-Rb-based perovskite films as shown in Figure 2. It is clearly seen that MA-based Sn-Pb perovskite films present the large grain size and large root mean square (r.m.s.) roughness of 16.1 nm; and some pinholes also coexist, which may originate from the uncontrollable crystallization of high-amount Sn components in the Sn-Pb perovskite system.^[15,23] These pinholes may cause current leakage and thus increase

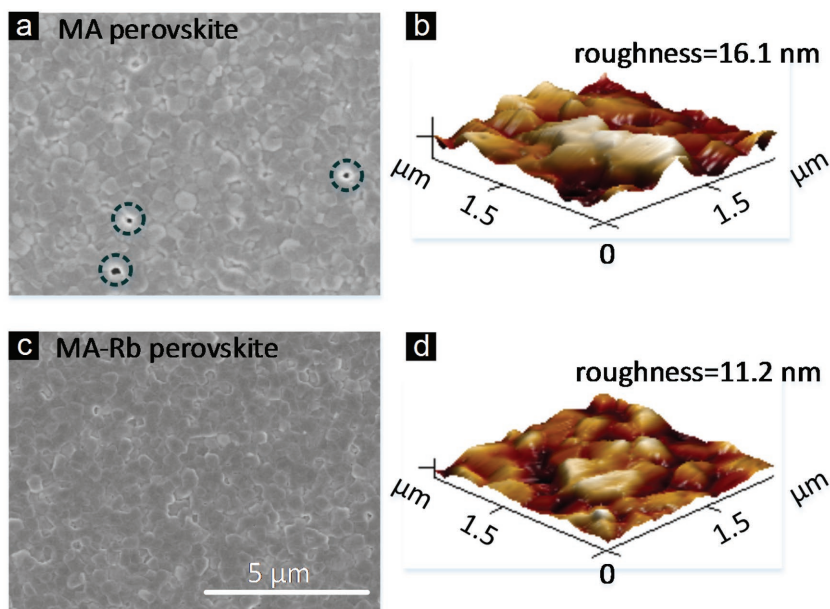


Figure 2. Top-view SEM images of a) $\text{MASn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ and c) $\text{MA}_{0.975}\text{Rb}_{0.025}\text{Sn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ perovskite films. The presence of pinholes in MA perovskite films is highlighted by circles. 3D AFM images of b) $\text{MASn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ and d) $\text{MA}_{0.975}\text{Rb}_{0.025}\text{Sn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ perovskite films show r.m.s. roughness of 16.1 and 11.2 nm, respectively.

dark current (as shown in Figure 1). Interestingly, through introducing small-amount Rb cation, MA-Rb-based perovskites show large grain size, pinhole-free, and smooth films (low r.m.s. roughness of 11.2 nm), indicating the controllable crystallization of MA-Rb Sn-Pb perovskite system. Meanwhile, we find that 2.5%-Rb-incorporation MA-Rb perovskites achieve the lowest roughness (Figure S5, Supporting Information, and Figure 2), which may contribute to the highest on/off ratio of MA-Rb perovskite PDs (Figure S2, Supporting Information). Moreover, we observe that phase segregation will present when more RbI_2 is added (Figure S6, Supporting Information), which would

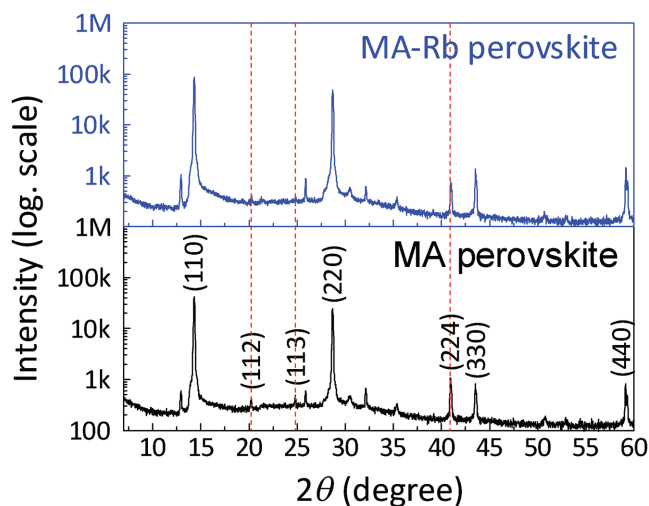


Figure 3. XRD patterns of $\text{MA}_{0.975}\text{Rb}_{0.025}\text{Sn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ (top) and $\text{MASn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ (bottom) perovskite thin films, respectively.

degrade device performances (Figure S2, Supporting Information).

X-ray diffraction (XRD) patterns were employed to investigate the crystallinity and orientation of fabricated Sn-Pb perovskite films. Remarkably, as shown in Figure 3 and enlarged XRD patterns in Figure S7 (Supporting Information), MA-Rb perovskites achieved significantly enhanced diffraction intensities of (110) plane by over two times compared with MA-based perovskites, suggesting the improvement of perovskite crystallinity. Meanwhile, it was found that intensities of (112), (113), and (224) planes of MA-Rb perovskite films were even reduced, which indicates the strengthened preferred orientation. In order to further characterize the preferred orientation, texture coefficient is introduced to compare MA and MA-Rb-based perovskite films. The texture coefficient of (110) plane relative to (112) plane (TC_{110}) can be derived by^[15,24]

$$\text{TC}_{110} = \frac{I_{110}/I_{110}^0}{I_{110}/I_{110}^0 + I_{112}/I_{112}^0} \quad (1)$$

where I_{110} and I_{112} are measured XRD intensities of (110) and (112) planes at the peak height, respectively. I_{110}^0 and I_{112}^0 are respective powder diffraction intensities of each plane. I_{110}^0 and I_{112}^0 are extracted from powder diffraction intensities of $\text{MASn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ single crystal (Figure S8, Supporting Information). The estimated TC_{110} for MA and MA-Rb-based perovskite films are 0.89 and 0.94, respectively. Compared with 25% Sn based $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskite films in our recent work ($\text{TC}_{110} = 0.88$),^[15] the slightly higher texture coefficient TC_{110} of 0.89 may result from the uncontrollable crystallization of higher Sn amount in Sn-Pb perovskite system^[23] and similar preferred orientation of Sn-based perovskites,^[25] which will induce pinholes and thus degrade device performances (as shown in Figures 1 and 2). Distinctively, small Rb amount incorporation will effectively modify the crystallization of 65% Sn based Sn-Pb perovskite system, and thus deposit dense film and enhance the orientation of the main plane. Strengthened preferred (110) plane orientation could be partially confirmed by the increased bandgap of MA-Rb perovskite films (Figure S9, Supporting Information), since energy gap for the (110) surface is larger than other surfaces according to the density functional theory calculation.^[26] Consequently, the introduction of small Rb amount into MA Sn-Pb perovskite system can effectively adjust the crystallization and thus induce increased perovskite crystallinity and strengthened preferred orientation, which is beneficial for efficient photodetection.

We will attempt to explore the underlying mechanism that Rb incorporation effectively facilitates the growth of high-quality Sn-Pb perovskite films with increased crystallinity and strengthened preferred orientation. While it is conventionally believed that adding small-size Rb into large-size cation (FA) based perovskites can tune tolerance factor, then stabilize perovskite phase, which is based on the thermodynamic stability

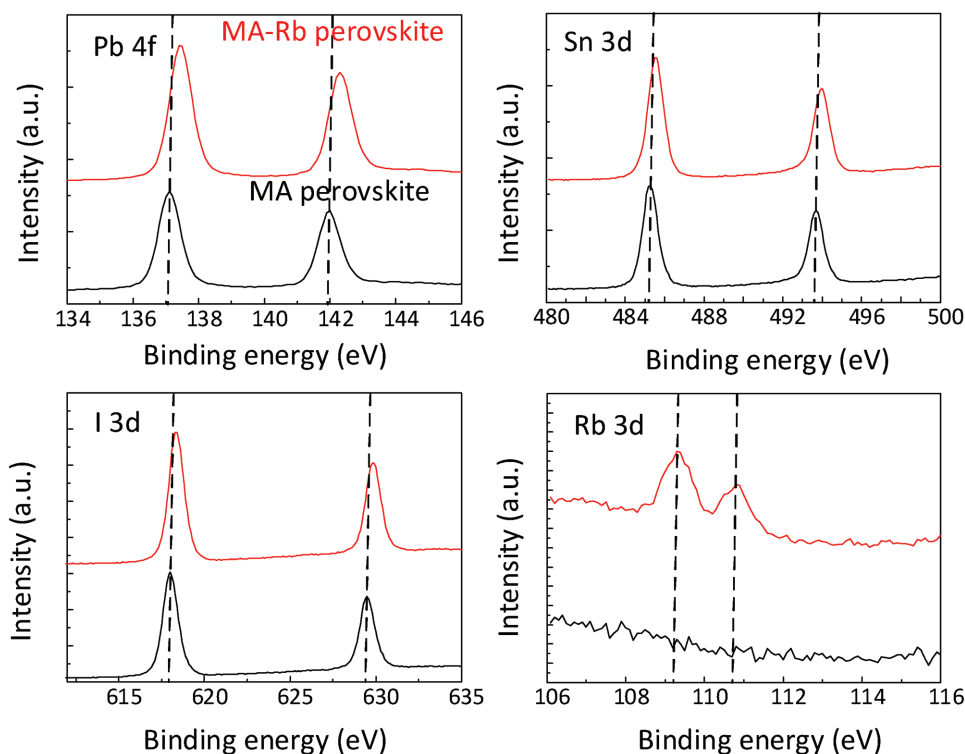


Figure 4. X-ray photoelectron spectra of $\text{MASn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ and $\text{MA}_{0.9}\text{Rb}_{0.1}\text{Sn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ perovskite films, respectively. Due to the small Rb amount (2.5%) and the equipment detection limit, $\text{MA}_{0.9}\text{Rb}_{0.1}\text{Sn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ was used to characterize the binding energy changes. In order to remove the influence of oxidation and surface contamination, both perovskite films were etched 10 nm before collecting data.

of the perovskite framework,^[19] we show very differently that Rb incorporation can effectively modify surface-energy-induced kinetic process during the growth of Sn-rich perovskites. Since the film orientation is related to the crystal surface energy, we calculated the surface energies of CsPbI_3 , RbPbI_3 , CsSnI_3 , and RbSnI_3 perovskites by employing ab initio simulation found in the Experimental Section. The surface energy changes are employed to study the influence of Rb incorporation on perovskites orientation (see details in the Supporting Information). We find that Rb introduction into $\text{CsPbI}_3/\text{CsSnI}_3$ perovskites ($\text{RbPbI}_3/\text{RbSnI}_3$) reduces the surface energies of all (110), (112), and (113) surfaces. Interestingly, Sn introduction into RbPbI_3 perovskites (RbSnI_3) reduces the surface energy of (110) plane, but meanwhile increases the surface energies of (112) and (113) planes. These findings indicate that Rb incorporation in Sn-rich Sn-Pb perovskite system can facilitate the perovskite growth in (110) plane and thus assist crystallization (strengthened preferred orientation and enhanced crystallinity), which are consistent with our results (Figure 3). It should be noted that we simplify the model replacing MA by Cs due to molecular-rotation-induced uncertainties of MA cations.^[27] The reduced surface energy for smaller A-site perovskites can be explained by the strong antibonding coupling at short Pb(Sn)–I bond. Considering the radius of Cs is smaller than that of MA, when Rb is incorporated into larger-lattice-constant MAPbI_3 , the reduction of surface energies is expected to be even larger.

In addition, the introduction of Rb cation in MA Sn-Pb perovskites will modify the perovskite structure. It will also influence the perovskite crystallinity and orientation. Intuitively,

considering steric effects, the effective Rb cation radius of 1.52 Å is smaller than the effective MA cation radius of 2.17 Å.^[28] Reduced cation radius, on the one hand, will reduce cubo-octahedral volume (reduced lattice constant can be confirmed by the increased 2θ angle in (440) plane as shown in Figure S7, Supporting Information) and thus increase the orbital interaction between Sn/Pb and I atoms.^[29,30] On the other hand, it will cause (Sn/Pb) I_2 octahedral tilting and induce MA^+ cation orientation change, and thus influence hydrogen bonding between MA^+ and (Sn/Pb) I_2 frame.^[30,31] According to the calculations of first principles within density functional theory, the conduction band bottom of MAPbI_3 perovskites mainly originates from the p orbitals of Pb, while the top of the valence band is derived from p orbitals of I.^[32] Therefore, stronger interaction between Sn/Pb and I atoms will tune the perovskite bandgap (Figure S9, Supporting Information) and influence other electronic properties (Figure 1).^[31] Meanwhile, the change of hydrogen bonding between cations and halide frames will alter the covalent/ionic character of Pb–I bonds, which also influence electronic properties of perovskites.^[30] As a consequence, in the case of MA-Rb Sn-Pb perovskite system, we speculate that Rb incorporation effectively adjusts the orbital interaction between Sn/Pb and I atoms as well as the degree of octahedral tilting of the (Sn/Pb) I_2 frame, which result into high symmetry (reduced energetic disorder) and thus increased crystallinity and strengthened preferred orientation.

To experimentally reveal the bonding change of Sn-Pb perovskites induced by Rb incorporation, we conducted X-ray photoelectron spectroscopy as shown in Figure 4. Evidently, Pb

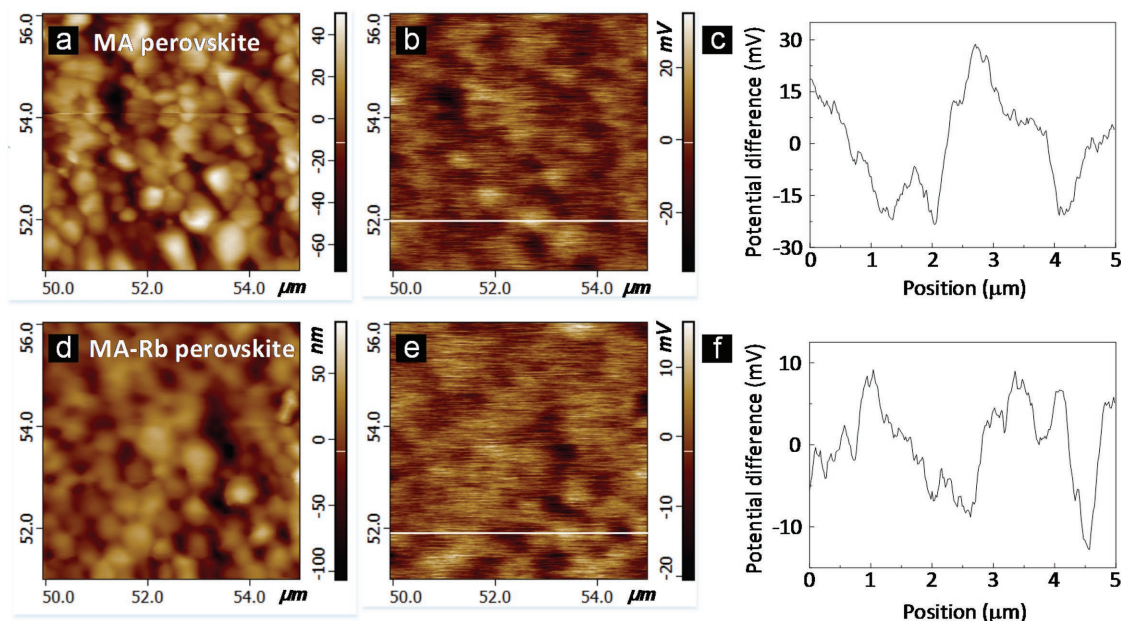


Figure 5. a,d) AFM images, b,e) corresponding surface potential maps, and c,f) cross-sectional profiles of MA perovskite film and MA-Rb perovskite film, respectively. MA perovskite film presents root-mean-square surface potential of 7.9 and 52 mV potential difference at the grain boundaries/grain interiors interface. MA-Rb perovskite film achieves root-mean-square surface potential of 4.2 and 21 mV potential difference between grain boundaries and grain interiors.

4f, Sn 3d, and I 3d peaks shifted toward higher binding energy, indicating the stronger interaction between Sn/Pb and I atoms. It further confirmed that Rb incorporation tunes the orbital interaction between Sn/Pb and I atoms, and the degree of (Sn/Pb) I₂ frame octahedral tilting. In addition, Urbach energy extracted from EQE spectra (Figure S4, Supporting Information) was introduced to characterize energetic disorder level of semiconductors. The Urbach energies of MA and MA-Rb-based perovskite films were 23.6 and 16.9 meV, respectively, indicating that MA-Rb-based Sn-Pb perovskites achieved lower-level energetic disorder.

2.3. Influence of MA-Rb Cation on Surface Potentials and Carrier Lifetime of Sn-Pb Perovskites

The influence of controllable crystallization of MA-Rb Sn-Pb perovskites on local surface potentials and charge carrier lifetime have been carefully investigated. Kelvin probe force microscopy was used to study local surface potentials that will affect photogenerated carriers transport and extraction.^[33] Figure 5 shows spatial morphology images, surface potential maps, and relevant cross-sectional profiles of MA and MA-Rb Sn-Pb perovskite films, respectively. It can be apparently seen that root-mean-square surface potential of MA-Rb Sn-Pb perovskite film was about 4.2 mV, which is lower than 7.9 mV surface potential difference of MA Sn-Pb perovskite film. Additionally, MA-Rb Sn-Pb perovskite film achieved a smaller potential difference of 21 mV at the grain boundaries/grain interiors interface compared with 52 mV potential difference of MA Sn-Pb perovskite film. The reduced surface potential difference indicates that the increased crystallinity and strengthened preferred orientation (MA-Rb Sn-Pb perovskites) reduce the barrier between grain

boundaries and grain interiors, which facilitate photogenerated current transport and extraction (Figure 1).^[34]

Time-resolved photoluminescence spectroscopy was used to study charge carrier lifetime change. Due to the limited spectral response of high-speed silicon detectors, the signals were collected at 880 nm and fitted with a monoexponential function. As shown in Figure S11 (Supporting Information), MA-Rb Sn-Pb perovskite film achieves a longer carrier lifetime as compared to MA-based Sn-Pb perovskite, indicating reduced nonradiative (trap-assisted) recombination, which should be ascribed to increased crystallinity and strengthened preferred orientation induced by Rb incorporation. In addition, the blue-shift of steady-state photoluminescence spectra (Figure S12, Supporting Information) further confirms that MA-Rb Sn-Pb perovskite film has a slightly larger bandgap that results from the strengthened preferred orientation, which is consistent with the bandgap derived from the absorbance spectra (Figure S9, Supporting Information).

2.4. Noise, LDR, Detectivity, and Transient Photocurrent Response

The controllable crystallization of MA-Rb Sn-Pb perovskite films on other figures of merit of PDs, including noise current, LDR, specific detectivity, and transient photocurrent response, will be discussed below in detail.

Regarding the LDR, the lower limit of LDR is determined by the noise current.^[3] As shown in Figure 6a, the lowest incident light intensity of MA-Rb Sn-Pb perovskites PDs is 1.32 pW cm⁻², which is lower than that of 6.6 pW cm⁻² for MA Sn-Pb perovskites PDs. The lower detectable optical power

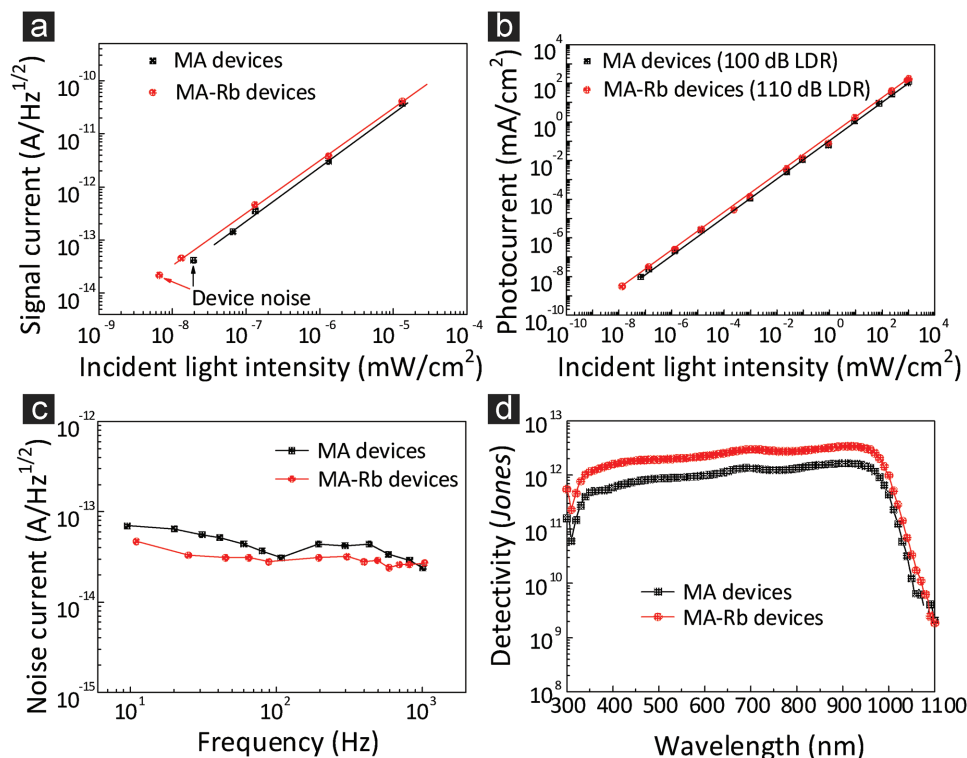


Figure 6. a) Signal current against incident light intensity, b) linear dynamic range plot (i.e., photocurrent density vs incident light intensity), c) noise current as a function of signal frequency, and d) specific detectivity versus spectral response range of MA perovskites and MA-Rb perovskites based PDs at the self-powered mode, respectively.

originates from the lower noise current, which results from lower thermal noise (increased shunt resistance as shown in Figure 1), reduced shot noise (reduced leakage current as shown in Figure 1), and negligible flicker noise (passivation of PC₆₁BM).^[20] The measured noise current shown in Figure 6c further confirmed that MA-Rb perovskites PDs achieved lower noise current, ascribing to dense film, increased crystallinity, and strengthened preferred orientation of MA-Rb Sn-Pb perovskite films. In addition, the lower LDR limit of 1.32 pW cm⁻² is two orders magnitude lower than that of Pb perovskite/quantum dots based PDs,^[5] one order magnitude lower than that of Pb perovskite/polymer based spectrally broad PDs,^[7] and at least three orders magnitude lower than that of quantum dots p-n heterojunction based PDs.^[21,35]

The upper LDR limit is determined by the lowest charge carrier mobility (PC₆₁BM) within PDs. Since PC₆₁BM dominates the upper limit of LDR, MA and MA-Rb-based Sn-Pb perovskite PDs achieved the similar highest optical power, as shown in Figure 6b. The measured highest light intensity of MA-Rb Sn-Pb perovskite PDs is about 1.05 W cm⁻². Therefore, LDR that defined by 10log(P_{upper}/P_{lower}) (P_{upper}/P_{lower} is the upper/lower limit of LDR) approached 110 dB for MA-Rb Sn-Pb perovskite PDs, which is, to the best of our knowledge, the highest value in Sn-Pb perovskite based PDs.^[18]

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

$$D^* = (AB)^{1/2} R/I_{noise} \quad (2)$$

where A is the detecting area of PDs, B is the bandwidth, R is the responsivity, and I_{noise} is the noise current. Specific detectivity D^* of MA and MA-Rb Sn-Pb perovskite PDs as a function of spectral response range is shown in Figure 6d. Clearly, MA-Rb Sn-Pb perovskite PDs achieved higher specific detectivity, resulting from the enhanced responsivity (Figure 1b) and the reduced noise current (Figure 6c). Additionally, MA-Rb Sn-Pb perovskite PDs achieved D^* exceeding 1.0×10^{12} Jones in near UV-vis-NIR region covering 340–1000 nm, which is better than commercial Ge spectrally broad PDs,^[2] small molecules based panchromatic PDs,^[36] inorganic semiconductor nanoparticles based PDs,^[21,35] and comparable with commercial Si PDs.^[2]

We also study the transient photocurrent response using a 532 nm 6 ps pulse width laser for evaluating the PDs ability to truthfully record an incident light signal. As shown in Figure 7a, self-powered MA-Rb Sn-Pb perovskite PDs achieved a rise time of 40 ns and a fall time of 468 ns. Through fast Fourier transform method shown in Figure S13 (Supporting Information), PDs achieved a 3 dB cutoff frequency of about 1 MHz. The frequency response using a square-wave voltage driven LED shown in the inset of Figure 7a presents that self-powered MA-Rb Sn-Pb perovskite PDs achieve a 3 dB cutoff frequency of 1 MHz, which is consistent with the value calculated from pulse laser determined transient photocurrent response. It should be noted that the response speed of our PDs is faster than most of inorganic semiconductor quantum dots based PDs (lower carrier mobility of quantum dots).^[2,35] Since the estimated RC time constant of our PDs was 308 ns (Figure S14,

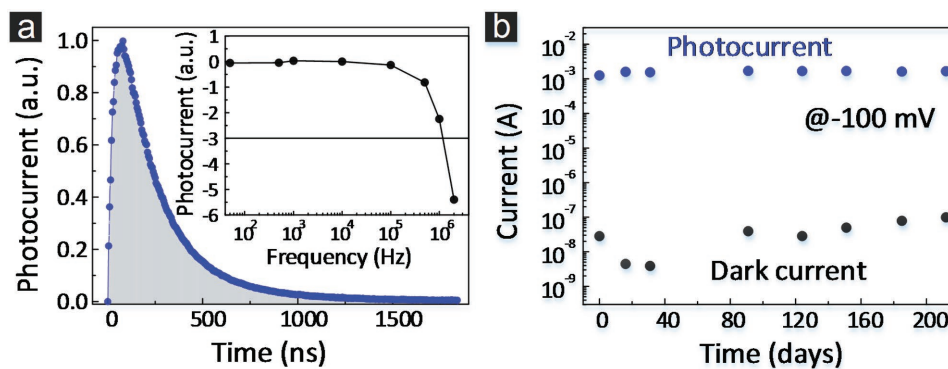


Figure 7. a) Transient photocurrent response of self-powered MA-Rb Sn-Pb perovskite PDs with a device area of 6 mm². Inset shows the frequency response of self-powered MA-Rb Sn-Pb perovskite PDs. b) Device stability of encapsulated MA-Rb Sn-Pb perovskite PDs.

Supporting Information) that is close to the fall time, it indicates that the transient photocurrent response in our case is governed by RC time constant. Additionally, MA-Rb Sn-Pb perovskite PDs achieved the smaller fall time compared with MA Sn-Pb perovskite PDs (Figure S15, Supporting Information), suggesting the reduced charge carrier accumulation within PDs induced by dense film, increased crystallinity, and strengthened preferred orientation. In order to meet some applications with faster response speed, RC time constant can be reduced, including reducing device area and circuit resistance.

In addition, we characterize the spectral photoresponse repeatability and device stability of PDs. The image shown in Figure S16 (Supporting Information) truly recorded that MA-Rb Sn-Pb perovskite PDs achieved repeatable photocurrent temporal response, indicating excellent photocurrent generation and extraction. More importantly, as shown in Figure 7b and Figure S17 (Supporting Information), encapsulated PDs presented the excellent device stability over 200 d storage. It suggests that high-quality MA-Rb Sn-Pb perovskites achieve superior material stability, and hole/electron interfacial layers (PEDOT:PSS and PC₆₁BM) that could passivate perovskites contribute to the long-term device stability, which are beneficial for practical uses.^[37]

3. Conclusions

We realize the controllable crystallization in MA Sn-rich perovskite system with the Sn content of 0.65 by introducing Rb cation. Our results show that the incorporation of Rb facilitates the growth of high-quality (smooth and dense) film with the improvements of increased crystallinity and strengthened preferred orientation, which reduce surface potential differences and increase charge carrier lifetime. The improvements can be explained that rubidium incorporation not only increases the orbital interaction between Sn/Pb and I atoms but also influences hydrogen bonding between MA⁺ and halides frame. Additionally, our theoretical results show that the reduced surface energy of (110) plane by the rubidium incorporation is also responsible for the improvements. Consequently, MA-Rb Sn-Pb perovskites PDs simultaneously achieve larger photocurrent and lower noise current. The optimized MA-Rb Sn-Pb perovskites PDs show UV-vis-NIR broad spectral detection (300–1100 nm), recorded linear dynamic range of 110 dB, high

responsivity, large detectivity of over 10¹² Jones covering 340–1000 nm and 3 dB cutoff frequency of about 1 MHz. These outstanding figures of merit of our UV-vis-NIR perovskite PDs make them highly promising for a broad range of applications, such as UV dosimetry and sensing, vis-light sensors, and NIR fluorescent imaging.

4. Experimental Section

Fabrication of MA and MA-Rb-Based Sn-Pb Perovskite Films: To prepare MA Sn-Pb perovskite precursors, 0.42 mmol PbI₂ (99.99%, TCI) and 1.2 mmol MAI (Dyesol) first dissolved in 1 mL mixed polar solvent of dimethylformamide and dimethyl sulfoxide (3:2 by volume). Regarding MA-Rb Sn-Pb perovskite precursors, 0.42 mmol PbI₂, 1.17 mmol MAI, and 0.03 mmol RbI (99.9%, Aldrich) dissolved in 1 mL mixed solvent. After stirred at room temperature for 1 h, solutions were mixed with 0.78 mmol SnI₂ (99.99%, Aldrich) and then stirred for 0.5 h before use. After that, both solutions were filtered by 0.22 μm syringe PTFE filters. Sn-Pb perovskite precursors were spin-coated on ITO/PEDOT:PSS substrates at the rate of 3000 rpm for 40 s. 300 μL toluene as the antisolvent was slowly dripped on spinning substrates at the first 10 s. Spin-coated thin films were annealed at 70 °C for 1 min and then 100 °C for 10 min for converting precursors to perovskite films. It should be noted that all the SnI₂ involved processes were conducted in a nitrogen-filled glove box to avoid oxidation.

Device Fabrication: The device architecture of Sn-Pb perovskite PDs is ITO/PEDOT:PSS/perovskites/PC₆₁BM/ZrAcac/Ag. ITO glass substrates were cleaned with deionized water, acetone, and ethanol, successively. PEDOT:PSS aqueous solution (Clevios P VP Al 4083) was spin-coated on the ultraviolet-ozone treated ITO substrates at 2000 rpm and annealed at 150 °C for 30 min. Then prepared samples were transferred to a nitrogen-filled glove box. Sn-Pb perovskite films were deposited on PEDOT:PSS substrates. Subsequently, 20 mg mL⁻¹ PC₆₁BM in chlorobenzene was spin-coated on perovskite films at 1200 rpm, followed by spin-coating 2 mg mL⁻¹ ZrAcac in isopropanol at 4000 rpm. Finally, 120 nm silver was deposited atop through the thermal evaporation under a vacuum of 10⁻⁴ Pa. The active area of Sn-Pb perovskite PDs was 0.06 cm².

Film Characterization: The top-view morphology images of Sn-Pb perovskites were characterized by Hitachi S4800 field-emission SEM. X-ray diffraction patterns of Sn-Pb perovskite films were characterized by BRUKER D2 PHASER. Surface potential difference was recorded by NT-MDT atomic force microscopy. The optical transmittance of MA and MA-Rb Sn-Pb perovskite films was measured by a home-made vis-NIR spectrophotometers. Urbach energy of Sn-Pb perovskites was extracted from the EQE spectra. X-ray photoelectron spectroscopy was conducted using Physical Electronics PHI-5802. Both MA and MA-Rb perovskite

films were etched 10 nm before collecting data in order to remove the influence of oxidation and surface contamination.

Device Characterization: Current densities against voltage and different wavelengths (responsivity) were recorded by a Keithley 2635 source meter with a light source setup of 1000 W xenon arc lamp. Linear dynamic range measurements were performed under different intensities of monochromatic light using ThorLabs metallic coated neutral density filters. The intensity of monochromatic light was measured by facility calibrated (Newport) Si photodetectors. Noise current of PDs was measured employing Stanford Research SR830 lock-in amplifier in the current measurement mode. The transient photocurrent response was conducted with a 532 nm 6 ps pulse width laser (130 μ J pulse⁻¹ maximum @400 Hz) integrated with an optical chopper and a 1 GHz Agilent DSO7104B digital storage oscilloscope. The frequency response was recorded with a 520 nm LED driven by HP 33120A function generator and a digital storage oscilloscope. All the measurements were conducted at room temperature in the ambient condition.

Simulations of Surface Formation Energies: The bulk and surface calculations were carried out via Vienna ab initio simulation package with the plane wave pseudopotential method.^[38] The wave functions were expanded in the plane wave up to a cutoff energy of 350 eV. The exchange-correlation function used was the general gradient approximation of Perdew, Burke, and Ernzerhof. The k-meshes (5 $\times$ 4 $\times$ 1), (3 $\times$ 3 $\times$ 1), and (3 $\times$ 2 $\times$ 1) were used in the calculations of (110), (112), and (113) surfaces of the cubic perovskite. Surface energy was calculated using slab model and defined by

$$E_{\text{surf}} = \frac{1}{2A} [E_{\text{total}}^{\text{slab}} - E_{\text{total}}^{\text{bulk}} + N(E_a + \mu_a)] \quad (3)$$

where $E_{\text{total}}^{\text{slab}}$, $E_{\text{total}}^{\text{bulk}}$, and E_a refer to the total energy of the slab, the total energy of the bulk, and the energy of extra atoms subtracted from bulk to form slab. μ_a was the chemical potential. The surface models and the calculated results are given in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

broad spectral photodetectors, low-bandgap Sn-rich perovskites, low noise currents, rubidium incorporation, ultraviolet–visible–near infrared detection

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