

## Article

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Achieving High-Quality Sn-Pb Perovskite  
Films on Complementary Metal-Oxide-  
Semiconductor-Compatible Metal/Silicon  
Substrates for Efficient Imaging Array

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## ABSTRACT

While Sn-Pb perovskites sensing near-ultraviolet-visible-near infrared light could be an attractive alternative to silicon in photodiodes and imaging, there have been no clear studies on such devices constructed on metal/silicon substrates hindering their direct integration with CMOS and silicon electronics. Typically, high surface roughness and severe pinholes of Sn-rich binary perovskites make them hardly fulfill requirements of efficient photodiodes and imaging. These issues cause inherently high dark current and poor (dark and photo-) current uniformity. Herein, we propose and demonstrate the room-temperature crystallization in the Sn-rich binary perovskite system to effectively control film crystallization kinetics. With experimental and theoretical studies of the crystallization mechanism, we successfully tune the density and location of nanocrystals in precursor films to achieve compact nanocrystals, which coalesce into high-quality (smooth, dense and pinhole-free) perovskites with intensified preferred orientation and decreased trap density. The high-quality perovskites reduce dark current and improve (dark and photo-) current uniformity of perovskite photodiodes on CMOS-compatible metal/silicon substrates. Meanwhile, self-powered devices achieve a high responsivity of 0.2 A/W at 940 nm, a large dynamic range of 100 dB and a fast fall time of 2.27  $\mu$ s, exceeding most silicon-based imaging sensors. Finally, a 6 $\times$ 6-pixels integrated photodiode array is successfully demonstrated to realize the imaging application. The work contributes to understanding the fundamentals of the crystallization of Sn-rich binary perovskites and advancing perovskite integration with Si-based electronics.

**KEYWORDS:** low-bandgap perovskites, Sn-Pb based perovskites, photodiodes, near-infrared imaging, room-temperature crystallization, CMOS-compatible metal/silicon substrates

Photodetectors for optical signal detection and their integrated pixel arrays constructed on CMOS for imaging harbor a variety of demanding applications, including flame detection, emerging Li-Fi-based wireless communication, visible imaging, artificial vision, biometric identification, machine vision, biomedical imaging, *etc.*<sup>1-4</sup> Conventionally, inorganic photoactive materials, such as crystalline silicon and III-V compound semiconductors, are predominantly employed for these applications.<sup>5, 6</sup> These inorganic semiconductors typically require ultrahigh vacuum, high temperature, rigorous fabrication processes, as well as restricted and costly substrates.<sup>7, 8</sup> Alternatively, hybrid lead halide perovskites can be robustly fabricated through simple low-temperature and solution-based processability. Meanwhile, they show impressive absorption coefficient (at least one order magnitude greater than silicon) and other outstanding optoelectronic properties, favoring their applications in photodetection and imaging.<sup>9-12</sup>

There have been several studies on lead halide perovskite photodiodes (PVSK-PDs) and metal-semiconductor-metal photodetectors.<sup>7, 13-18</sup> Forwards, low-bandgap Sn-rich binary PVSK-PDs offer the advantage of expanding the spectral response to the near-infrared region beyond the detection limit of Pb-based PVSK-PDs. Until now, most studies of Sn-rich binary PVSK-PDs are constructed on indium tin oxide (ITO)/glass substrates,<sup>19-23</sup> and not on CMOS-compatible metal/silicon substrates, which are particularly important for bridging their uses in the mainstream CMOS and silicon electronics.<sup>5</sup> Moreover, the integration of these single-unit devices into a pixel array for imaging has not been reported. Overall, the realization of low-bandgap Sn-rich binary PVSK-PDs on the metal/silicon substrates and demonstration of pixel integration and image capture will invoke their advances towards practical applications.

Critically, rough surfaces and pinholes of photoactive layers will increase dark current

and even impair (dark and photo) current uniformity of pixel arrays, degrading the image quality.<sup>24, 25</sup> Because of these issues, the reported Pb-based PVSK-PDs array on silicon substrates showed tiny photovoltage and thus low on/off ratio.<sup>26</sup> Regarding Sn-based perovskites, due to the stronger Lewis acidity of  $\text{Sn}^{2+}$  *versus*  $\text{Pb}^{2+}$  to MAI that causes their fast formation, these perovskites normally suffer from high surface roughness and severe pinholes hardly compatible with pixel arrays.<sup>27-29</sup> Consequently, it is highly desirable to demonstrate approaches to grow smooth and pinhole-free Sn-rich binary perovskite films for efficient PVSK-PDs and integrated pixel arrays on the metal/silicon substrates.

In this work, we demonstrate efficient low-bandgap Sn-rich binary PVSK-PDs on CMOS-compatible metal/silicon substrates, and further realize the integration of a 6×6-pixel array as conceptual demonstration for the imaging application. By introducing the room-temperature crystallization in the Sn-rich binary perovskite system, we effectively control the density and location of nanocrystals in Sn-rich binary precursor films. Ultimately, we realize the growth of compact nanocrystals, which thermally coalesce into high-quality (smooth, dense and pinhole-free) Sn-rich binary perovskite films with intensified preferred orientation and decreased trap density. These features beneficially contribute to the reduction of dark current and the improvement of (dark and photo) current uniformity of Sn-rich binary PVSK-PDs. Overall, the work contributes to the fundamentals on controlling the crystallization of Sn-rich binary perovskites as well as advancing their direct integration with Si electronics.

## RESULTS AND DISCUSSION

Low-bandgap Sn-rich binary PVSK-PDs are fabricated on metal/Si substrates with the device structure of Si/ 3-mercaptopropyltrimethoxysilane (MPS)/ metal/  $\text{MoO}_3$ / poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)/ Sn-rich

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4 binary perovskites/ phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM)/ zirconium  
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6 acetylacetonate (ZrAcac)/ transparent thin metal films/ MoO<sub>3</sub> capping layer. It is  
7  
8 important to note that although thermally deposited metal films on MPS treated Si  
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10 substrates can have a low root-mean-square (r.m.s.) roughness of 1.7 nm, there is a  
11  
12 challenging issue that thermal-evaporated metal films typically form vertical needle-  
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14 type islands with very sharp shapes and the high height of 32.2 nm. (see Figure S1)  
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16 Such sharp metal islands will easily penetrate into perovskite films and their  
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18 interconnections will induce severe recombination and chemical reactions in-  
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20 between.<sup>30</sup> Through incorporating the MoO<sub>3</sub>/PEDOT:PSS bilayer, the morphology is  
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22 considerably smoothened with the r.m.s roughness of 1.2 nm. More importantly, the  
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24 island height dramatically reduces to 12.8 nm suppressing the penetration into  
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26 perovskites from bottom metals. (The detailed discussion on the MoO<sub>3</sub>/PEDOT:PSS  
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28 bilayer can be found in Supporting Information Note S1)  
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33 **High-quality Sn-rich binary perovskites.** With the smooth carrier extraction  
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35 layer/metal/Si substrate structure, we demonstrate the high-quality crystalline films  
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37 through the formation of compact nanocrystals induced by room-temperature  
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39 crystallization (nucleation and growth) in Sn-rich binary perovskite precursor films.  
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41 The room-temperature crystallization time of Sn-rich binary precursor films is defined  
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43 by the time between the anti-solvent washing process and post-annealing treatment.  
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45 Given an appropriate crystallization time, freshly anti-solvent washed Sn-rich binary  
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47 perovskite precursor films gradually turn into black, indicating room-temperature  
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49 crystallization in Sn-rich binary perovskites, which facilitate the control of  
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51 crystallization kinetics (to be discussed later). The film roughness against different  
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53 times of crystallization is shown in Figure 1a. Manifestly, the r.m.s. roughness of Sn-  
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55 rich binary perovskite films is significantly reduced from 31 nm at the crystallization  
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time of 0 s to 8 nm at the time of 60 s. Meanwhile, Sn-rich binary perovskite films show gradually reduced pinholes and become pinhole-free when the time reaches 60 s, as shown from scanning electron microscope (SEM) images in Figure 1b. Therefore, our results show that through controlling room-temperature crystallization time, we can achieve smooth, dense and pinhole-free Sn-rich binary perovskite films.

**Device performance optimization.** Benefiting from the roughness reduction and pinhole elimination of crystalline Sn-rich binary perovskites, we can diminish the dark current due to the reduction of recombination current, confirmed by the reduced value of the saturation current density of PVSK-PDs (Figure S2). The uniformity of dark current and photocurrent will also be improved, which is essential for a pixel array.<sup>25</sup> The improved performances can be confirmed from the performance statistics (dark current density, photocurrent density and on/off ratio) as shown in Figure 1c. PVSK-PDs with the Sn-rich binary perovskites formed at the crystallization time of 0 s show the dark current density between  $6.4 \times 10^{-4}$  and  $6.4 \times 10^{-7}$  A cm<sup>-2</sup>, suggesting the inferior uniformity with a high deviation. As crystallization time increases, not only dark current density of PVSK-PDs reduces, but also the uniformity of dark current improves. At the crystallization time of 40 s, the dark current density reduces to as low as  $(2.8 \pm 0.81) \times 10^{-7}$  A cm<sup>-2</sup> and the photocurrent density increases to  $(9.2 \pm 0.47) \times 10^{-3}$  A cm<sup>-2</sup>. Finally, through finely controlling the room-temperature crystallization time, Sn-rich binary PVSK-PDs show the optimized on/off ratio with improved value and superior uniformity at the time of 40 s. These improvements are essential for efficient photodiodes and integrated pixel arrays.

We further enhance the near-infrared responsivity through the cavity structure consisted of metal/Si substrates and top transparent metal electrodes. The optimization of top transparent metal electrodes can be found in Note S2 (Supporting Information). As

shown in Figure 2a, the theoretical device absorption (see the model in Methods) presents the absorption tuning, and significantly achieves near-infrared absorption enhancement by increasing the perovskite thickness from 300 to 400 nm. The experimental results are shown in Figure 2b. The responsivity experiences over two-fold increase from 0.09 to 0.2 A/W at the wavelength of 940 nm. The enhanced responsivity in the near-infrared region is promising for emerging applications, such as biometric identification, machine vision, and biomedical imaging.

**Mechanism of growing high-quality films through room-temperature compact nanocrystals.** Smooth, dense and pinhole-free films are expected to originate from the compact nanocrystal formation induced by room-temperature crystallization in Sn-rich binary perovskite precursor films. Initially, it is expected that a few nuclei appear in Sn-rich binary perovskite precursors, which could compose of soft complexes of organic components coordinated with inorganic ones.<sup>31-34</sup> Our theoretical results show that there is a strong Sn-O ionic bond between SnI<sub>2</sub> and dimethyl sulfoxide (DMSO) with 0.550 eV dissociation energy as shown in Figure 3a and Figure S3. The strong Sn-O ionic bond makes uncoordinated organic components remain in precursor films, which impedes the formation of new nuclei when precursor films are freshly treated by anti-solvent washing (*i.e.* the room-temperature crystallization time at 0 s). These pre-existed nuclei (see Figure 3g(i)) would continue the crystal growth when thermal annealing is immediately employed. The isolated island-like crystals shown in Figure 3c shall be formed in the rapid crystal growth from the relatively less numbers of nuclei. Meanwhile, the thermal annealing at the crystallization time of 0 s will quickly remove residual solvents and thus induce severe reactions between uncoordinated organic components and SnI<sub>2</sub>, increasing the surface roughness.<sup>23</sup> Therefore, Sn-rich binary perovskite precursors at the crystallization time of 0 s will produce pinhole, rough and

discontinuous films (see Figure 3c).

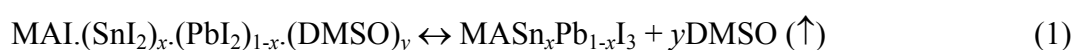
Importantly, Sn-rich binary perovskite precursor films can crystallize at room temperature. We observe that light-brown Sn-Pb binary perovskite precursor films after anti-solvent washing gradually turned into black and smooth films (Figure S4). This suggests the spontaneous nucleation and growth in Sn-Pb binary perovskite precursor films. Theoretically, the room-temperature nucleation is expected from Sn-based complexes due to the strong I-Sn ionic bonding between MAI and  $\text{SnI}_2$ . Our simulation results show that the dissociation energy of the I-Sn ionic bonding is indeed very large with a value of 0.676 eV as shown in Figure 3b and Figure S3. According to our theoretical studies through the LaMer model,<sup>35</sup> after treated by the anti-solvent washing (*i.e.* the room-temperature crystallization time > 0 s), it could be anticipated that supersaturated precursors on the top film surface favor both the generation of new nuclei and then their rapid completion of the crystal growth. Meanwhile, precursors on the bottom surface may have the relatively lower concentration than that on the top surface and thus dominantly prefer to grow crystals from the pre-existed few nuclei (see Figure 3g(ii)).

Experimentally, we observe that massive small-size nanocrystals appear on the top surface of precursor films (Figure 3f) when precursor films have the enough crystallization time, confirming enough nuclei generation on the top surface and rapid crystal growth. Meantime, the relatively large-size nanocrystals on PEDOT:PSS substrates confirm that the pre-existed few nuclei located on substrates continue crystal growth. Interestingly, as shown in Figure 3c-e (crystallization time at 0 s, 10 s and 60 s) and Figure S5 (crystallization time at 20 s and 40 s), the crystallization of top-surface precursor films completes within ~10 s, while that of bottom-surface precursor films lasts around 40 s. Therefore, resultant Sn-rich binary perovskite films show isolated

crystals (Figure 3c), large voids and discontinuous films (Figure 1b) at the short crystallization time of less than 10 s, and present undesirable voids (Figure 3d and Figure S5) when the time is between 10 s and 40 s. Importantly, when the crystallization time is greater than 40 s, the formation of compact nanocrystals in precursor films is achieved (see Figure 3g(iii)). After flash annealing, compact nanocrystals thermally coalesce with each other to produce smooth, dense and pinhole-free perovskite films (Figure 3e). Consequently, we conclude that the formation of compact nanocrystals in Sn-rich binary perovskite precursor films is essential for growing high-quality perovskite films.

The nanocrystal formation dynamic in precursor films is studied by the absorption ratio, which is determined by the light absorption intensity of precursor films at 750-nm wavelength over that of corresponding post-annealed films, as shown in Figure S6. The absorption ratio sharply increases the value from the room-temperature crystallization time of 0 s to about 40 s (*i.e.* increased numbers and sizes of isolated nanocrystals) and shows the stabilized value afterward (*i.e.* the formation of compact nanocrystals). The tendency of the absorption ratio *versus* the crystallization time generally corresponds to that of surface roughness and pinholes (see Figure 1a and 1b). In Figure 1a, roughness dramatically reduces at the initial crystallization time from 0 s to about 50 s and then stabilizes at the longer time, and pinholes at different crystallization times are shown in Figure 1b. These further confirm that high-quality Sn-rich binary perovskite films correlate strongly with the formation of compact nanocrystals in precursor films. Inspired by these findings, we can employ the room-temperature crystallization to control the density and location of nanocrystals in Sn-rich binary perovskite precursor films and eventually achieve compact nanocrystals, which coalesce with each other to form high-quality films after thermal annealing.

The plausible chemical mechanism of room-temperature crystallization of Sn-rich binary perovskites would be briefly discussed below. As shown in Figure S7, the C-H stretching vibration from solvents (3300-3500 cm<sup>-1</sup>) significantly reduces with the increased crystallization time from 0 to 10 s, and gradually drops when the time increases to 40 s. Meanwhile, the S=O stretching vibration from DMSO-based intermediates (1018-1007 cm<sup>-1</sup>) gently decreases during the crystallization time from 0 to 10 s, and almost disappears at the time of 40 s. Therefore, after freshly treated by anti-solvent washing (*i.e.* the crystallization time at 0 s), it could be anticipated that pre-existed Sn-Pb binary perovskite nuclei, residual solvents and DMSO-based intermediates coexist in precursor films.<sup>31-33</sup> When the crystallization time increases, due to the fast removal of residual solvents from the top-surface precursor films (Figure S7), a large amount of new Sn-Pb binary perovskite nuclei would be expected to form and grow into small nanocrystals (Figure 3g(ii)). Meanwhile, pre-existed nuclei on the bottom surface of precursor films grow into large nanocrystals driven by the consumption of DMSO-based intermediates (Figure 3f). The released solvent molecules from bulk will dissolve top-surface perovskite nuclei and small nanocrystals, and then new DMSO-based intermediates will be formed (process I). Sequentially, the top-surface precursor films experience the removal of solvents, new nuclei generation and growth (process II). These two processes (process I and II) are spontaneously repeated several times at room temperature driven by the slow removal of DMSO from precursor films (see Equation 1).



Finally, after solvents are removed, room-temperature crystallization of Sn-rich binary perovskite precursor films with pinhole-free morphology would be achieved (Figure 3f and 3g(iii)).

Based on the above theoretical and experimental understanding, we summarize the growth mechanism of high-quality films through room-temperature compact nanocrystal formation in the Sn-rich binary perovskite system. As shown in Figure 3g, freshly anti-solvent washed Sn-rich binary perovskite precursor films with insufficient nuclei (Figure 3g(i)) will result in isolated nanocrystals, large voids and then discontinuous films after thermal annealing (Figure 1b and Figure 3c). Through controlling the room-temperature crystallization time, new massive nuclei appear on top surfaces of precursor films and rapidly grow to small-size nanocrystals. Meanwhile, pre-existed nuclei on substrates experience the slow growth and grow to large-size nanocrystals. Both contribute to the formation of compact nanocrystals (Figure 3g(iii) and Figure 3f), which will significantly coalesce with each other to form smooth, dense and pinhole-free films after thermal annealing (Figure 3e).

**Influences of room-temperature crystallization time on orientation and trap density of Sn-rich binary perovskites.** The influence of room-temperature crystallization time on crystallinity and orientation of Sn-rich binary perovskites is studied by X-ray diffraction (XRD) as shown in Figure 4a. The intensity of main (110) planes of Sn-rich binary perovskites are gradually reduced as the crystallization time increases, as shown in Figure 4a and Figure S8. The slightly higher (110) plane intensity at the shorter crystallization time can be explained by the thicker crystals (Figure 3c-e) that experienced thermal-induced vertical-growth from relatively insufficient nucleation sites.<sup>32</sup> Significantly, the full width at half maximum of (110) planes remain the same value, indicating same crystal sizes at various crystallization time according to Scherrer equation.<sup>36</sup> The same crystal sizes at the longer crystallization time shall be ascribed to thermal-induced parallel coalescence of small-size crystals with each other (Figure 3e-f), indicting the effectiveness of flash annealing that enlarges grain size and

reduces grain boundaries.<sup>37</sup>

The texture coefficient (TC) is introduced to characterize the preferred orientation of a material. As shown in Figure 4b, the texture coefficient of (110) plane relative to (112) plane ( $TC_{110}$ ) of Sn-rich binary perovskite films increases as the room-temperature crystallization time increases, indicating the intensification of the preferred orientation of (110) plane, further confirmed by grazing incidence wide-angle X-ray scattering (GIWAXS) patterns that Sn-rich binary perovskites at the crystallization time of 40 s achieve the increased intensity compared with perovskites at the crystallization time of 0 s (Figure S9). The intensified preferred orientation confirms the effectiveness of the room-temperature crystallization in growing Sn-rich binary perovskites. The trap density of Sn-rich binary perovskites are determined by the trap-filled limited voltages of hole-only devices as shown in Figure S10 and summarized in Figure 4c.<sup>38, 39</sup> Clearly, Sn-rich binary perovskite films with longer room-temperature crystallization time favor the film formation with low trap density and thus improve film quality.

**Figures of merit of Sn-rich binary perovskite photodiodes.** Figures of merit of Sn-rich binary PVSK-PDs at the optimized crystallization time of 40 s (Figure 1c), including external quantum efficiency (EQE), noise current, dynamic range, specific detectivity, and transient photocurrent response, will be discussed in detail as follows.

The optimized Sn-rich binary PVSK-PDs can achieve a broad spectral response from 300 nm to 1100 nm as shown in Figure 5a. Specifically, PVSK-PDs present ~ 50% EQE in the visible region and over 20% EQE in the near-infrared region (780-970 nm). Notably, the high EQE covering the near-infrared region is better than most commercial silicon-based imaging sensors, which are potential applications in mobile phone-based facial recognition and surveillance cameras.<sup>40</sup> Regarding dynamic range behavior, Sn-

rich binary PVSK-PDs achieve an dynamic range of 100 dB (see Figure S11), which is better than that of commercial imaging sensors ( $\sim 60$  dB) and is comparable to state-of-the-art wide-dynamic-range imaging sensors ( $\sim 100$  dB).<sup>41-44</sup>

Interestingly, PVSK-PDs show almost frequency-independent characteristics in noise current as shown in Figure 5b. The results suggest the ignorable flicker noise in our devices, which can be explained by fullerene passivation on Sn-rich binary perovskites and reduced trap density (Figure 4c).<sup>7</sup> Notably, the ignorable flicker noise means that only the sum of thermal noise and shot noise contribute to the total noise of Sn-rich binary PVSK-PDs, which is experimentally confirmed in Figure 5b.

Meanwhile, Sn-rich binary PVSK-PDs achieve specific detectivity  $D^*$  exceeding  $10^{11}$  Jones in near ultraviolet-visible-near-infrared region covering 360-985 nm as shown in Figure 5c. Specific detectivity  $D^* = (AB)^{1/2} \cdot EQE \cdot \lambda / (1240 I_{noise})$ , where  $A$  is the work area,  $B$  is the bandwidth,  $\lambda$  is the wavelength, and  $I_{noise}$  is the measured noise current. The results show that Sn-rich binary PVSK-PDs on CMOS-compatible metal/silicon substrates demonstrate comparable specific detectivity with commercial Ge broadband photodetectors,<sup>6</sup> small molecule-based panchromatic photodetectors,<sup>45</sup> inorganic semiconductor nanoparticle-based photodetectors, and approach the value of Si photodetectors.<sup>46</sup>

We also investigate the temporal photocurrent response, as shown in Figure 5d. The self-powered Sn-rich binary PVSK-PDs on metal/Si substrates demonstrate a rise time of 90 ns and a fall time of 2.27  $\mu$ s. The fall time of our Sn-rich binary PVSK-PDs is lower than most of inorganic semiconductor quantum dots based photodetectors (lower carrier mobility of quantum dots) and is comparable with Sn-Pb binary PVSK-PDs constructed on ITO/glass substrates.<sup>6, 19, 20, 46</sup> The fast response characteristics of our devices can meet the application requirements in high-speed imaging, in-flight object

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4 recognition, time-of-flight camera, *etc.*<sup>6</sup> Additionally, we characterize the photocurrent  
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6 repeatability. Figure S12 truthfully records that Sn-rich binary PVSK-PDs achieve  
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8 repeatable photocurrent response, implying efficient photocurrent generation and  
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10 extraction. Importantly, apart from fabricating PVSK-PDs on Cu/Si substrates, we  
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12 successfully deposited devices on Al/Si substrates through the approach of compact Sn-  
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14 rich binary perovskite nanocrystals and achieved very good performances (see Figure  
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16 S13).  
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20 **Pixel integration and image capture.** We demonstrate the ability of image capture of  
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22 the metal/Si-substrate based Sn-rich binary PVSK-PD pixel array by integrating 6×6  
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24 pixels with each pixel active area of 1 mm × 1 mm, as shown in Figure S14. The  
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26 photocurrent uniformity of these pixels is of importance, since photocurrent non-  
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28 uniformity degrades the image quality captured by pixels.<sup>42</sup> As shown in Figure 6a and  
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30 Figure 6b, these 6×6 Sn-rich binary PVSK-PDs pixels present normalized photocurrent  
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32 from 0.7 to 1.0, suggesting the excellent photocurrent uniformity, which originates  
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34 from high-quality perovskite films produced by the room-temperature formation of  
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36 compact nanocrystals. Finally, we put a hollow ‘+’ sign between our pixel array and  
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38 the incident light. The figure of the desirable object would be brought by the incident  
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40 light and then captured by our Sn-rich binary PVSK-PDs pixel array, as shown in Figure  
41  
42 6c. Vividly, our PVSK-PDs pixels can truthfully record the hollow ‘+’ sign. The  
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44 successful demonstration of pixel integration and image capture employing the  
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46 metal/silicon-substrate-based Sn-rich binary PVSK-PDs would promote their further  
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48 development towards practical applications.  
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## 54 CONCLUSIONS

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58 Efficient low-bandgap Sn-rich binary PVSK-PDs on CMOS-compatible metal/silicon  
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substrates are successfully demonstrated through effectively controlling film crystallization kinetics by the approach of room-temperature crystallization in the Sn-rich binary perovskite system. With the theoretical and experimental studies, we control the density and location of nanocrystals in Sn-rich binary perovskite precursor films to produce compact nanocrystals, which coalesce into high-quality Sn-rich binary perovskite films. Equally important, crystalline perovskites also show intensified preferred orientation and decreased trap density. With these properties, PVSK-PDs achieve improved (dark and photo) current uniformity and optimized on/off ratio (enhanced value and uniformity). By optimizing the device with the optical cavity structure, we realize the spectral response tunability and enhance near-infrared responsivity. Self-powered devices achieve a high responsivity of 0.2 A/W at 940 nm, a large dynamic range of 100 dB and a fast fall time of 2.27  $\mu$ s, exceeding most silicon-based imaging sensors. At last, a 6 $\times$ 6 pixels array with excellent photocurrent uniformity is conceptually demonstrated for the imaging application. Consequently, our work, as the starting point for future research of perovskite-based pixel array directly constructed on metal/Si substrates (with CMOS compatibility), will contribute to emerging applications of perovskite technologies such as visible imaging, biometric identification, machine vision, and biomedical imaging.

## METHODS

**Preparation of Sn-rich binary perovskite films.** Sn-Pb binary perovskite precursors were prepared by mixing 1.17 mmol MAI (Greatcell Solar Limited), 0.03 mmol RbI (99.9%, Sigma-Aldrich), 0.78 mmol SnI<sub>2</sub> (99.99%, Sigma-Aldrich) and 0.42 mmol PbI<sub>2</sub> (99.99%, TCI) into 1 ml mixed solvent of dimethylformamide and DMSO. Before use, precursors were stirred for ~20 min at room temperature, and then filtered by 0.22  $\mu$ m PTFE filters. Sn-rich binary perovskite films were fabricated through the revised anti-solvent method,<sup>47</sup> and toluene was selected as the anti-solvent. Specifically, precursors were spin-coated on substrates at the speed rate of 5000 rpm. 300  $\mu$ l toluene was slowly dripped on spin-coated precursors at the first 15 second. The anti-solvent washed precursor films on substrates remained spinning for desirable time to fulfil the room-temperature crystallization. Notably, optimizing the crystallization time is essential for the formation of compact nanocrystals, which will coalesce into high-quality films after perovskite precursor films were annealed at 180 degree Celsius for 20 s.

**Fabrication of photodiodes and pixel integration.** Silicon substrates were consecutively treated by ultrasonic cleaning using acetone and ethanol. After dried by the industrial Nitrogen gas, silicon substrates were treated by 30 mM 3-mercaptopropyltrimethoxysilane (J&K Chemical) dissolved in toluene. 3-mercaptopropyltrimethoxysilane was employed as a self-assembled monolayer to modify surface properties of silicon substrates, in which methoxysilane groups covalently bond with hydroxyl groups of SiO<sub>2</sub> surfaces, and terminal thiol groups covalently bond with desirable metal layers.<sup>48</sup> Desirable metal bottom electrodes with different patterns were thermally evaporated by the deposition rate of 1 Å/s, followed by the deposition of MoO<sub>3</sub> (10 nm). After that, PEDOT:PSS (Clevios™ P VP AI 4083) was spin-coated atop and annealed at 120 degree Celsius for 30 min. High-quality Sn-

rich binary perovskite films were fabricated by the room-temperature compact nanocrystal formation. Subsequently, 20 mg/ml PC<sub>61</sub>BM in chlorobenzene was spin-coated on perovskite films at 1200 rpm, followed by spin-coating 2 mg/ml ZrAcac in isopropanol at 4000 rpm. Finally, 10 nm top transparent electrodes with different patterns (the deposition rate is 2 Å/s) were deposited atop through the thermal evaporation under a vacuum of 10<sup>-6</sup> Torr. Bottom and top electrodes of 6×6 pixels were fabricated using a slit-array pattern with 1 mm width and 0.5 mm pitch. Active areas of single-unit Sn-rich binary PVSK-PDs and array pixels were 0.06 and 0.01 cm<sup>2</sup>, respectively. It should be noted that all the SnI<sub>2</sub> involved processes were conducted in a nitrogen-filled glove box to avoid oxidation.

**Film characterization.** Top-view morphology images of Sn-rich binary perovskites were characterized by Hitachi S4800 field-emission SEM. X-ray diffraction patterns of Sn-rich binary perovskite films were characterized by BRUKER D2 PHASER. GIWAXS measurements were performed by Rigaku SmartLab 9kW X-ray diffractometer. Surface roughness was recorded by NT-MDT atomic-force microscopy (AFM). Fourier-transform infrared spectroscopy (FTIR) was recorded by JASCO FT/IR-6600. The optical transmittance and reflectance of perovskite films were measured by a home-made visible-near infrared spectrophotometer. Sheet resistance of thin transparent electrodes was measured using a four-point probe, a voltage meter and a current meter.

**Device characterization.** Current density against voltage of Sn-rich binary PVSK-PDs were recorded by a Keithley 2635 source meter. EQE was measured by Enlitech QE-R3011. Dynamic range measurements were performed under different light intensities using Zolix metallic coated neutral density filters. Noise current was measured employing Platform Design Automation, Inc. NC300. The temporal photocurrent

response was conducted with a 532 nm pulse laser and a digital oscilloscope. The light intensity was measured by facility calibrated (Newport) Si photodetectors. All the measurements were conducted at room temperature in the ambient condition.

**Surface energy calculations.** The first-principles density-functional theory calculations were performed to calculate the dissociation energy of DMSO (or MAI) on the surface of  $\text{SnI}_2$  and  $\text{PbI}_2$  using the VASP software.<sup>49</sup> The slab models of the  $\text{SnI}_2$  and  $\text{PbI}_2$  surfaces with slab/vacuum thickness of 10/6 Å and 15/6 Å respectively, are constructed (see in Figure S3). The dissociation energies are obtained by calculating the energy difference between the total energy of DMSO (or MAI)-adsorbed surface and the sum of total energies for bare surface and DMSO molecule (or MAI). The atoms at bottom two layers of the slab were fixed during atomic optimization. The results show that DMSO forms a strong Sn-O bond on  $\text{SnI}_2$  surface, while DMSO is physically adsorbed on  $\text{PbI}_2$  surface. Moreover, MAI has a stronger I-Sn ionic bond on  $\text{SnI}_2$  surface.

**Device absorption simulations.** An optical model was implemented to simulate the field distribution inside perovskite devices, by solving the Maxwell's equation using finite-difference method.<sup>50</sup> With this model, the normalized absorption spectra and free-carrier generation rates of devices can be obtained. Realistic refractive indexes were adopted in the simulation, which were measured from ellipsometry (*VASE* J.A. Woollam Co., Inc.). For the normalized absorption spectra simulation, light intensity of illumination under different wavelengths ranging from 300 nm to 1000 nm were assumed to be uniform, in order to analyse the absorption capacities of the devices.

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## ASSOCIATED CONTENT

Authors declare no competing financial interest.

### Supporting Information

**Supporting Information Available:** This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

AFM images of Cu/MPS/Si and PEDOT:PSS/MoO<sub>3</sub>/Cu/MPS/Si, saturation current density, optimization of top transparent metal electrodes, dissociation energy calculations, SEM images, absorption ratio, FTIR spectra, GIWAXS patterns, trap density estimation, dynamic range, repeatable temporal response, and an image of our photodiode array.

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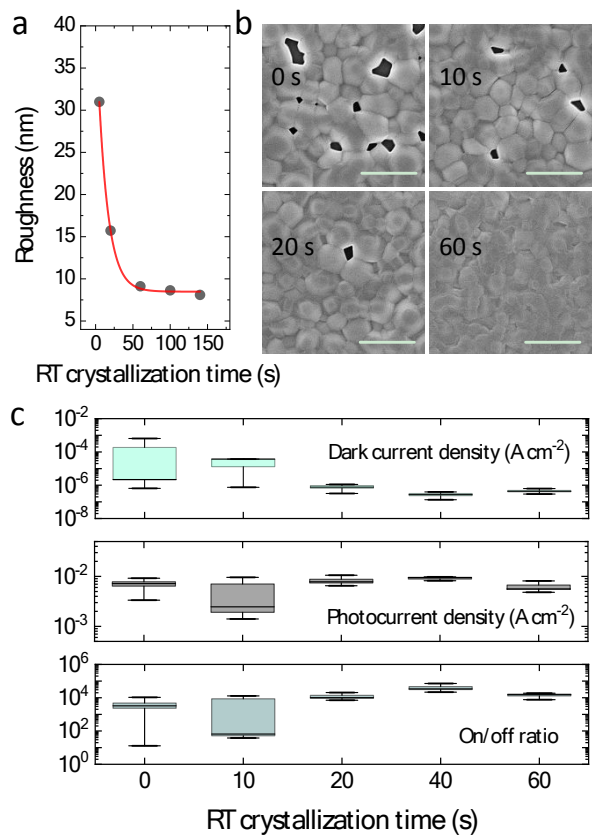


**Figure 1.** (a) r.m.s. roughness of Sn-rich binary perovskite films against the room-temperature (RT) crystallization time. The red line is a guide to the eye. (b) SEM images of Sn-rich binary perovskite films processed by various room-temperature crystallization time. All scale bars are 1  $\mu m$ . (c) Dark current density, photocurrent density and on/off ratio (photocurrent to dark current) of Sn-rich binary PVSK-PDs against various crystallization time of Sn-rich binary perovskite films. These devices were constructed on Cu/silicon substrates and worked at the bias of -10 mV.

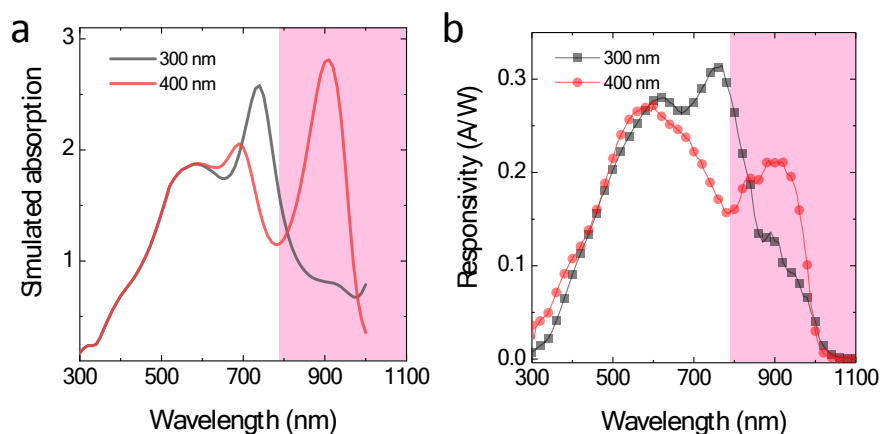


**Figure 2.** (a) Simulated absorption of Sn-rich binary PVSK-PDs as a function of perovskite thickness. (b) Experimental near-infrared responsivity spectra of Sn-rich binary PVSK-PDs. The light red blocks show near-infrared regions.

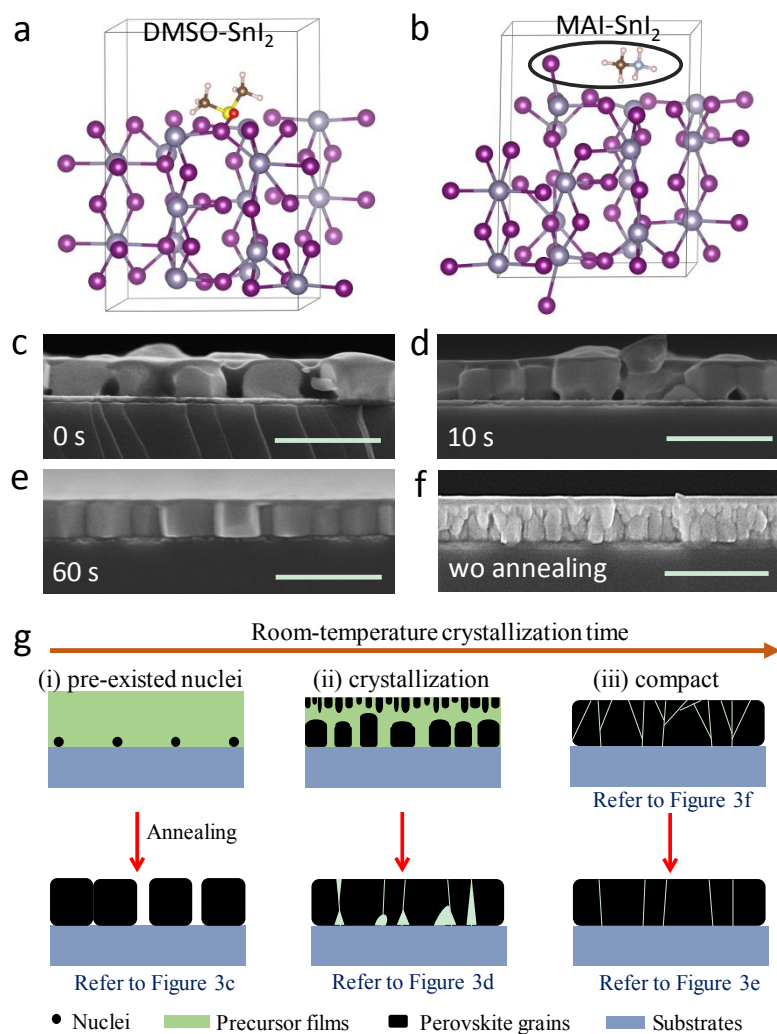


**Figure 3.** Schematic illustrations of the bonding between SnI<sub>2</sub> and DMSO (a), and the bonding between SnI<sub>2</sub> and MAI (b). MAI is highlighted by the oval. Cross-sectional SEM images of perovskite films with the various time of room-temperature crystallization: (c) 0 s, (d) 10 s, and (e) 60 s. After room-temperature crystallization, these precursor films were treated by thermal annealing to produce resultant films. (f) Cross-sectional SEM image of the Sn-rich binary perovskite precursor film with room-temperature crystallization for enough time. The film was not treated by thermal annealing. All films were protected by the PC<sub>61</sub>BM layer. All scale bars are 1  $\mu$ m. (g) The schematic diagram of growing high-quality perovskite films in the Sn-rich binary perovskite system.

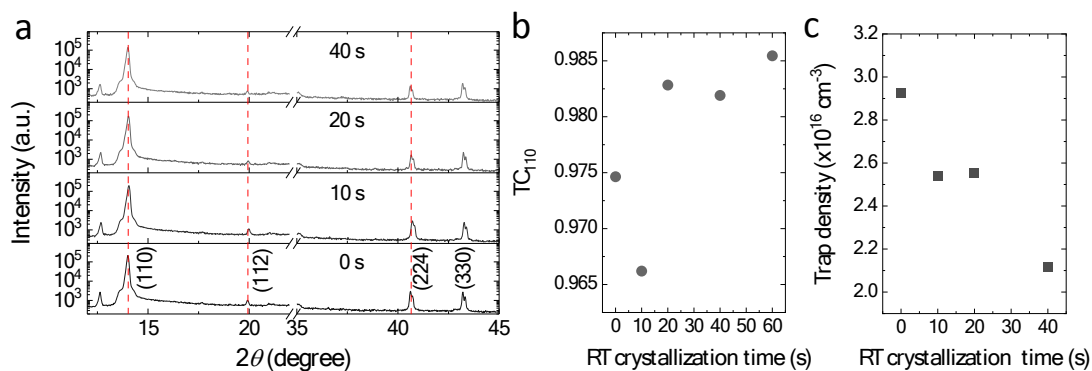


**Figure 4.** (a) XRD patterns of Sn-rich binary perovskite films against the room-temperature crystallization time. (b) The texture coefficient evolution of (110) plane relative to (112) plane ( $TC_{110}$ ) of Sn-rich binary perovskite films as a function of the room-temperature crystallization time. (c) Trap density of Sn-rich binary perovskite films against the room-temperature crystallization time.

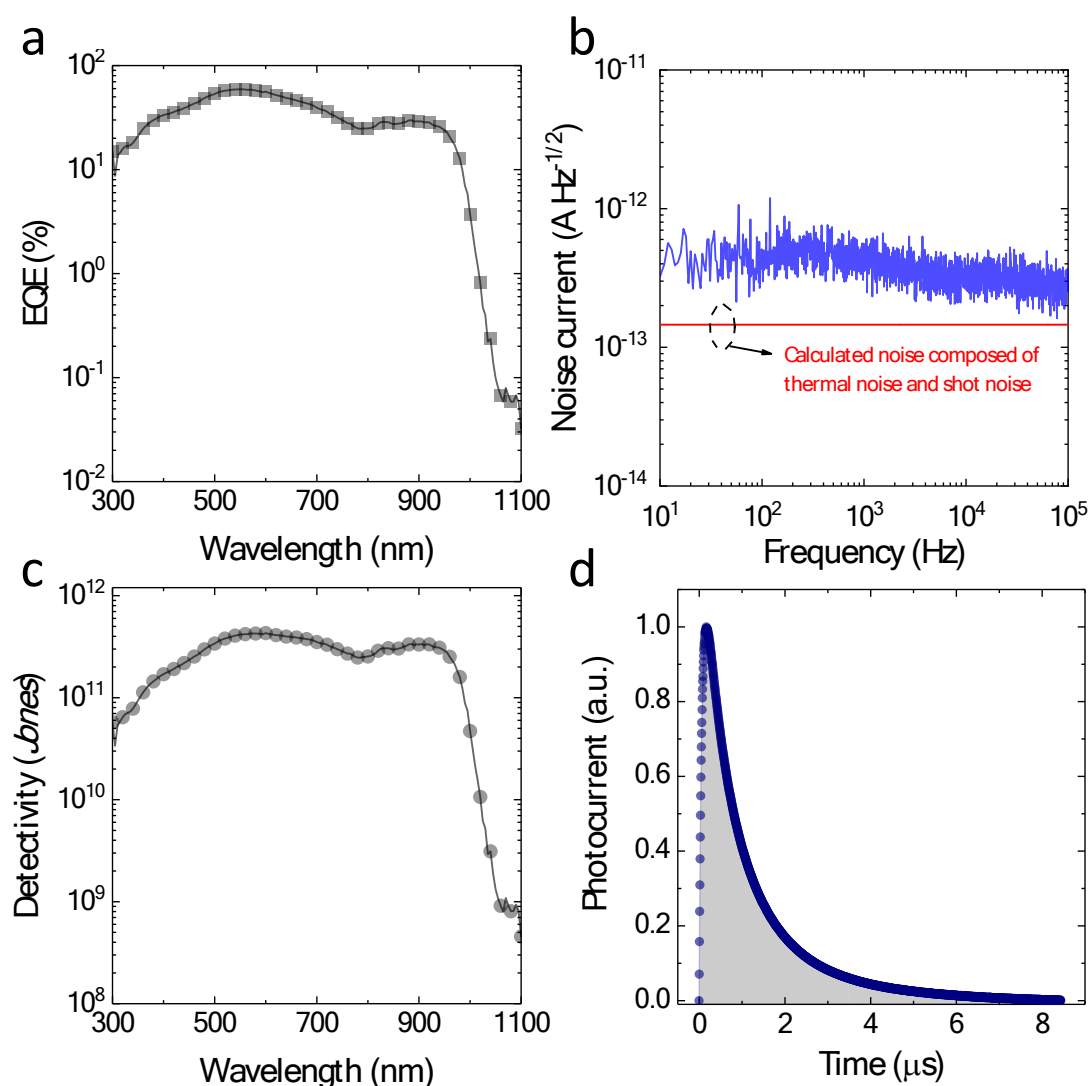


**Figure 5.** Figures of merit of Sn-rich binary PVSK-PDs constructed on Cu/silicon substrates. (a) EQE against the wavelength of incident light. (b) Noise current as a function of signal frequency. The theoretically calculated noise composed of thermal noise and shot noise was plotted for comparison. (c) Specific detectivity *versus* the spectral response range. (d) Temporal photocurrent response. Devices with the area of  $6 \text{ mm}^2$  were operated at the self-powered mode.

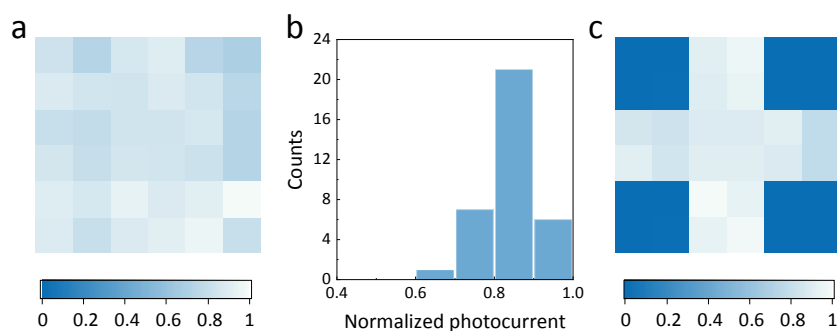


**Figure 6.** (a) Photocurrent uniformity of 6×6 Sn-rich binary PVSK-PDs pixels. (b) Photocurrent distributions of 36 Sn-rich binary PVSK-PDs pixels. (c) The image of a ‘+’ sign naturally captured by our Sn-rich binary PVSK-PDs imaging array with 6×6 pixels.

Table of Contents Graphic

