A sensitive self-powered perovskite photodetector via noise suppression with poly(vinylidene fluoride–trifluoroethylene) doping for defect passivation†

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The rapid advancement of self-powered perovskite photodetectors (PDs) in recent years has been hindered by numerous defects present in solution-processed perovskite polycrystalline films, significantly impacting device performance. Of particular concern is the influence of these defects on device noise, a critical parameter directly affecting detector sensitivity. This study proposes the incorporation of poly(vinylidene fluoride–trifluoroethylene) (PVT) additives into FA0.9MA0.05Cs0.05PbI3 perovskite precursor solutions to alleviate defect formation and enhance detector sensitivity. By optimizing the PVT concentration to 0.05 mg L\(^{-1}\), the photodetector (PD) demonstrates remarkable improvement, achieving a low noise power spectral density (0.1 pA Hz\(^{-1/2}\)) and dark current density (2.12 nA cm\(^{-2}\)) at zero bias. The device exhibits a notable decrease in defect density by an order of magnitude through the concurrent passivation of shallow-level defects with PVT. Additionally, the PD shows a high specific detection rate (D* = 2.8 \times 10^{13} \text{ Jones}) at 700 nm, accompanied by a linear dynamic range exceeding 10\(^{13}\) jones. This research not only advances our understanding of noise suppression mechanisms but also unveils the potential application of high-sensitivity PDs for real-time heart rate monitoring, showing promise for significant advancements in human health monitoring technology.

Introduction

Organic–inorganic hybrid perovskites have attracted widespread attention in applications of solar cells, light-emitting diodes, and photodetectors, due to their excellent optoelectronic properties.\(^1\)–\(^9\) Especially in the field of photodetection, self-powered perovskite photodetectors (PDs) play an important role in healthcare, bioimaging and other fields.\(^10\)–\(^11\) Among them, lead halide perovskite materials show high photocurrent and good stability, and have been widely studied in the field of photodetection.\(^12\)–\(^13\)

Despite the high photocurrent of lead halide PDs,\(^14\) it is unfortunate that perovskite polycrystalline films prepared by spin-coating have high density of defect states, leading to severe device noise, which seriously affects the device’s detection sensitivity.\(^15\)–\(^17\) These defects trap photon-generated carriers and cause carrier number fluctuations. These will cause a lot of noise and reduce the sensitivity of the device. To improve the sensitivity of perovskite PDs, much research has been reported over the past few years. Wang et al. introduced P(VDF-TrFE) (poly(vinylidene fluoride–trifluoroethylene)) doping to enhance the response of perovskite MAPbI\(_3\)/Si heterojunctions and introduced the pyro-phototronic effect.\(^18\) Instantaneous temperature changes in MAPbI\(_3\)/PVT films generate a pyroelectric potential. This promotes effective carrier separation and transport through the heterojunction, improving the response wavelength and device response. Zhang et al. proposed a strategy to passivate the defects using Lewis-base additive urea.\(^19\) Urea passivation enhances perovskite crystallinity and reduces defect states. The response of perovskite PDs is significantly improved by such performance enhancements.

In recent years, FA\(_{0.9}\)MA\(_{0.05}\)Cs\(_{0.05}\)PbI\(_3\) perovskites are known for their excellent photovoltaic properties and robust stability, making them particularly attractive for various commercial and practical PD applications. However, perovskite polycrystalline films suffer from a large number of shallow energy level defects, such as organic cation vacancies (V\(_F\)), iodine vacancies (V\(_I\)) and lead vacancies (V\(_Pb\)).\(^20\)–\(^22\) These defects result in an increase in the 1/f noise at low frequencies.\(^23\) In this study, a fluorinated long-chain polymer additive strategy is proposed to reduce device defects. The use of PVT to coat perovskite grains and form hydrogen and coordination bonds with perovskite can passivate shallow energy level defects in perovskite films. A series of PVT: FA\(_{0.9}\)MA\(_{0.05}\)Cs\(_{0.05}\)PbI\(_3\) self-powered PDs by
Results and discussion

As a transparent organic polymer, PVT has a wide range of applications in microelectronics such as sensors, memory, photovoltaic electronics and artificial skin.\textsuperscript{24–29} PVT was introduced to effectively passivate film defects in perovskite films.\textsuperscript{30–32} In order to determine the optimal PVT addition concentration, a comparative test was carried out. As shown in Fig. S1 (ESI†), 0.05 mg mL\textsuperscript{-1} was proved to be an optimal concentration with the lowest dark current, while more PVT in perovskite films may prevent carrier transport due to its insulating properties, resulting in a low photocurrent. The increasing degree of dark current dispersion in the device is shown in the inset. This may be due to a reduction in film uniformity caused by excessive PVT addition. The concentrations of the following PVT are all 0.05 mg mL\textsuperscript{-1}. There is no significant change in the absorption curves shown in Fig. S2 (ESI†). This shows that PVT does not affect the UV-visible absorption properties of the film. Surface passivation was obtained with the addition of PVT, as demonstrated in Fig. 1a and b, which display scanning electron microscope (SEM) images of the original sample of perovskite and the PVT-treated perovskite sample. The SEM images clearly show that the films containing PVT have larger grains. This may be due to PVT-assisted nucleation and growth during the crystallisation process of perovskites.\textsuperscript{33,34} Large grains help to reduce thin film grain boundary defects to increase charge carrier transport capacity. By fitting X-ray diffraction (XRD) data (as shown in Fig. S3, ESI†), the crystallinity of the films was obtained. As shown in Fig. 1c, the yellow and blue colours in the bar graph represent the crystallinity data of the original and PVT-added films, respectively. Crystallinity increased from 87.98% to 99.71% for PVT passivation films. This suggests that we have produced perovskite polycrystalline films with better properties. The detailed PVT doping perovskite film characterisation was then performed by transmission electron microscopy (TEM) and is shown in Fig. 1d. This confirms that the amorphous PVT molecule exists at grain boundaries. It forms a cross-linked structure of the adjacent perovskite. The high-resolution TEM (HRTEM) image of the PVT-coating perovskite is shown in the inset. The thickness of the PVT film at the grain boundary is about 3 nm. And through the HRTEM image, it can be observed that there is no obvious lattice fringe on the other side of the perovskite film. The above results show that the PVT-added perovskite polycrystalline films have larger grains and stronger crystallinity. Density functional theory (DFT) calculations were carried out to understand the interactions between PVT and perovskite. Fig. 2a shows the electrostatic potential (ESP) of PVT. The region containing the fluorine atom is red and has a strong negative charge. The electron-rich regions drive the coordination with the uncoordinated Pb\textsuperscript{2+} and significantly improve the electrostatic attraction between PVT and perovskite.\textsuperscript{35,36} Furthermore, –CF\textsubscript{2} can form covalent bonds with organic cations.

![Fig. 1](https://example.com/fig1.png)

**Fig. 1** SEM images of perovskite films without (a) and with (b) PVT addition, (c) crystallinity of perovskite films without and with PVT, (d) TEM of perovskite films with PVT.

![Fig. 2](https://example.com/fig2.png)

**Fig. 2** (a) ESP diagram of PVT, (b) V\textsubscript{FA}, (c) V\textsubscript{MA} and (d) V\textsubscript{Pb} formation energy on the FA\textsubscript{0.9}MA\textsubscript{0.05}Cs\textsubscript{0.05}Pbl\textsubscript{3} perovskite surface, (e) the formation energy of perovskite defects without and with the addition of PVT, (f) the diagram of the complexation between PVT and FA\textsubscript{0.9}MA\textsubscript{0.05}Cs\textsubscript{0.05}Pbl\textsubscript{3} perovskites.
In order to understand the interaction mechanism between PVT molecules and perovskites at the atomic level, we have analysed their interactions. It shows that PVT can change the formation energy of $V_{FA}$, $V_{I}$ and $V_{FA}$ in perovskite. Fig. 2b–d show the defect formation energy on the $FA_0.9MA_0.05Cs_{0.05}PbI_3$ perovskite surface. The locations of the defects are marked in the diagram by red curves. Fig. 2e shows a comparison of the formation energy of perovskite defects without and with the addition of PVT. After PVT modification, the formation energy of $V_{pbe}, V_{I}$ and $V_{FA}$ increased by 1.63, 1.37 and 1.99 times under the passivation of $-CF_2$, respectively. This work reveals that the defect formation energy of $V_{vax}$ on the surface of the $FA_0.9MA_0.05Cs_{0.05}PbI_3$ perovskite is notably higher compared to $V_{pbe}$ and $V_{I}$, suggesting a higher difficulty in $V_{vax}$ formation. Notably, the pronounced increase in $V_{FA}$ formation energy is attributed to an intermolecular N–H⋯F hydrogen bond between $-CF_2$ and FA.¹⁷–⁴² This observation is illustrated in Fig. 2f, depicting the complexation between PVT and $FA_0.9MA_0.05Cs_{0.05}PbI_3$ perovskites, as confirmed by DFT calculations. The red curve displays the diagram of the complexation between PVT and perovskites. It indicates that PVT has the ability to inhibit the formation of three types of defects.

PVT addition suppresses shallow energy level defects in $FA_0.9MA_0.05Cs_{0.05}PbI_3$ films. Next, the perovskite PDs in this study have the same device structure as the regular solar cell n–i–p structure of the ITO glass/SnO$_2$ layer/$FA_0.9MA_0.05Cs_{0.05}PbI_3$ (without and with PVT)/spiro-OMeTAD/Ag structure. The photodetection capability of the device has been evaluated using a laboratory designed test system. The PDs were tested at zero bias under illumination of 0.004 W cm$^{-2}$ (685 nm). Fig. 3a and c shows the current as a function of time under serial cycles. Fig. 3b and d show enlarged views of the dark current in the cyclic curve. As can be seen, the photocurrent shows a noticeable difference while the dark current is dramatically inhibited in the target device. The introduction of PVT endowed the ability to inhibit the dark current by about two orders of magnitude and to maintain a high photocurrent of around 100 µA. The small change in photocurrent shows that the addition of a moderate amount of PVT does not affect the carrier transport of the film under light conditions. However, the addition of PVT significantly suppressed dark current generation. This results in a significant improvement in the switching ratio of the PD. Fig. 3e shows the noise spectral density of the device obtained by Fourier transforming the dark current in the time domain.⁴³ The noise spectral density of the PVT passivated PD is reduced by two orders of magnitude compared to the original device. This reduces the PD’s noise power spectral density from 30 pA Hz$^{-1/2}$ to 0.1 pA Hz$^{-1/2}$. At low-frequency operation ($f < 1000$ Hz), the presence of shallow defects in the energy level can lead to a large amount of 1/f noise in the PDs.⁴⁴ However, PVT additives contribute to the formation of high quality perovskite films due to the stable and reliable intermolecular N–H⋯F hydrogen bonds between $-CF_2$ and FA. This prevents the formation of shallow energy level defects. The reduction of the noise signal significantly improves the detection performance of the device under weak light conditions. We tested the temperature-dependent dark current of perovskite PDs and derived the activation energy of the charge traps that induce the dark current from the slope of ln(dark current) versus 1/$T$. The results of this test and the DFT calculations are consistent with PVT being effective in passivating shallow energy level defects in $FA_0.9MA_0.05Cs_{0.05}PbI_3$ films. As shown in Fig. 3f, the device without PVT exhibited a very shallow trap with an activation energy ($E_A$) of 3.47 ± 0.4 meV. The energy levels of the films are so shallow that they produce large carrier fluctuations at room temperature, which accounts for the very high noise levels in these films. Fig. 3g shows a consistent reduction in trap density across the perovskite films upon PVT passivation; particularly evident is a 20-times reduction in defect density observed primarily near the top surface interface of $FA_0.9MA_0.05Cs_{0.05}PbI_3$ with hole transporting layers. PVT inhibits the formation of defects at the upper interface. The trap density of states (tDOS) spectra in Fig. S4 (ESI†) show that the shallow trap density was reduced by an order of magnitude, while the difference in the deep trap states may be negligible. The density of the shallow trap was significantly reduced by surface passivation with PVT, again demonstrating that this defect is mainly located at the top surface of $FA_0.9MA_0.05Cs_{0.05}PbI_3$ with hole transporting layers. Among them, the 1/f noise of the device is effectively reduced by the reduction of shallow energy level defects. It is well known that high noise levels can reduce the detection performance of photodetectors. This study concludes that the passivation of shallow energy level traps on the film by PVT can reduce the 1/f noise in perovskite PDs by 2 orders.

Fig. 4a shows a schematic of the device structure of PVT: $FA_0.9MA_0.05Cs_{0.05}PbI_3$ perovskite PDs with Glass/ITO/SnO$_2$/ $FA_0.9MA_0.05Cs_{0.05}PbI_3$ with PVT/spiro-OMeTAD/Ag. To illustrate the improvement of PD performance, the specific detectivity ($D^*$) of PDs is calculated using the following equation:⁴⁵–⁴⁷
\[
D^* = \frac{R}{(2qJ_d)^{1/2}} = EQE \times \frac{\lambda}{1240(2qJ_d)^{1/2}}
\]
where \( J_d \) is the dark current density, \( q \) is the elementary electron charge, and \( \lambda \) is the wavelength. EQE is the external quantum efficiency of the device as determined by experiment. Fig. S6 (ESI†) shows the EQE variation curves of the PDs with and without PVT. The EQE value of the PD fabricated by introducing PVT into the precursor exceeds 80% with 0 V bias in the region from 300 to 800 nm. Furthermore, at wavelengths from 700 to 800 nm, the EQE values are significantly higher than those of the original device. The results show that the photovoltaic conversion performance of the device with PVT is significantly improved. Fig. 4b illustrates \( D^* \) performance calculated from the EQE data, showing a corresponding improvement with the addition of PVT. The largest \( D^* \) of 2.8 \( \times 10^{13} \) jones was obtained at 700 nm. The excellent detection capability of the PVT doped PDs can be assigned from the passivation of the defects at shallow energy levels of the device by the PVT. This makes it easier to extract and transport the carriers and also suppresses noise generation. At the same time, high specific detection rates are important for the practical application of photodetectors. The linear dynamic range (LDR) is an important performance parameter that characterises the carrier extraction ability.

The LDR of the device can be obtained from eqn (2), where \( J_{ph} \) is the device photocurrent.

\[
\text{LDR} = 20 \log \frac{J_{ph}}{J_d}
\]  

Fig. 4 (a) Schematic of the device structure of PVT: FA0.9MA0.05Cs0.05PbI3 perovskite PDs, (b) the specific detectivity and (c) linear dynamic range of photodetectors with and without PVT, (d) response time of photodetector with PVT.

The photocurrent values of the PDs were measured as a function of light intensity under illumination and are shown in Fig. 4c. Benefiting from defect passivation, it is clear that the PVT doping detector has a very wide LDR, with a detectable minimum intensity of 0.58 \( \times 10^{-6} \) W cm\(^{-2}\). From the excellent optical and electrical properties discussed above the LDR of the PVT-doping device is 101 dB, which is much higher than that of the device without PVT (94 dB). And under illumination, the photocurrent rose to a high value and then gradually reached a stable value, which might be due to the charge recombination mechanism. The large LDR gives the photodetector the ability to detect over a wide range of incident light intensities, a prerequisite for high fidelity imaging applications. The response speed describes a PD’s ability to track rapidly changing light signals. It is defined as the time taken for the photocurrent to rise from 10% to 90% of the peak value and to fall from 90% to 10% as the rise time and fall time respectively. Fig. 4d shows the rise time and fall time of the PVT-added device to be 16.3 \( \mu \)s and 23.9 \( \mu \)s respectively. The short response time means a quick response speed for the optimized device. The regular beating of the heart results in periodic changes in blood flow. Among them, oxygenated haemoglobin (HBO\(_2\)) and deoxygenated haemoglobin (Hb) have different light absorption capacities, and their light absorption varies mostly between 600 nm and 700 nm.\(^{50}\) PVT passivated perovskite-based PDs were used for pulse testing in this study. As shown in Fig. S7a (ESI†), a narrow wavelength detector (from 600 to 700 nm) was obtained with the attached filters. As shown in Fig. S7b (ESI†), a volunteer’s finger is placed between the 685 nm LED and the photodetector. Due to the difference in light absorption between HBO\(_2\) and Hb, the PD can produce regular detection signals as shown in Fig. S7c (ESI†). The heart rate was estimated to be 70 beats per minute. These results indicate that PVT:FA0.9MA0.05Cs0.05PbI3 perovskite PDs have a promising application in bioassays.

Conclusions

In summary, this study reported a method for the preparation of dense and homogeneous films by the addition of PVT to the FA0.9MA0.05Cs0.05PbI3 perovskite precursor solution. PVT was introduced at the grain boundaries and proved to passivate the shallow energy level defects of the FA0.9MA0.05Cs0.05PbI3 perovskite films through hydrogen bonds between \( -CF_2 \) and FA\(^+\). As a result, the reduction of shallow energy level defects suppresses the 1/f noise of the PD. The addition of the optimum value of 0.05 mg L\(^{-1}\) to the PVT will have a significant impact on the detection performance of the PD. After the optimisation, the noise current of the PD is 0.1 pA Hz\(^{-1/2}\) at zero bias and \( D^* \) is 2.8 \( \times 10^{13} \) jones at 700 nm. At the same time, the minimum detectable light intensity of the PD is 0.58 \( \times 10^{-6} \) W cm\(^{-2}\) and LDR is over 101 dB. The PDs with a vertical structure show a fast response time with a rise time of 16.3 \( \mu \)s and a fall time of 23.9 \( \mu \)s. A fingertip pulse testing system was also developed based on a PVT:FA0.9MA0.05Cs0.05PbI3 perovskite PD. This work provides a promising approach to improving the performance of PDs for use in medical detection systems.

Author contributions

G. T. and M. W. directed the research project and supervised the experimental design. Y. L. and Z. L. conceived the idea and performed most of the experiments. Y. H. and X. L. assisted in...
device fabrication and film measurements. Z. Z. contributed to the first-principles calculation. H. Y. assisted in analyzing the data. Y. L., Z. L., Y. S. and M. W. wrote the paper. All authors discussed the results and commented on the manuscript.

Conflicts of interest
There are no conflicts to declare.

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References
Communication


