

Interface Engineering of High-Performance Perovskite Photodetectors Based on PVP/SnO₂ Electron Transport Layer

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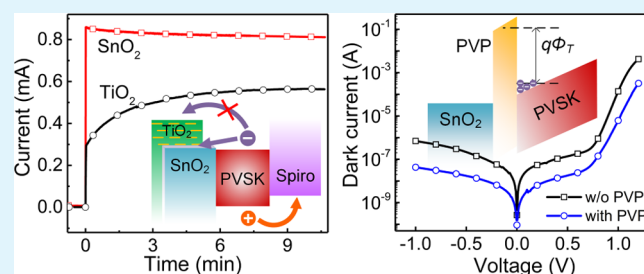
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S Supporting Information

ABSTRACT: Hybrid organic–inorganic perovskites have attracted intensive interest as active materials for high-performance photodetectors. However, studies on the electron transport layer (ETL) and its influence on the response time of photodetectors remain limited. Herein, we compare the performances of perovskite photodetectors with TiO₂ and SnO₂ ETLs, especially on the response time. Both photodetectors exhibit a high on/off current ratio of 10⁵, a large detectivity around 10¹² Jones, and a linear dynamic range over 80 dB. The SnO₂-based perovskite photodiodes show ultrahigh response rates of 3 and 6 μ s for the rise and decay times, respectively. However, photodetectors with TiO₂ ETLs have low responsivity and long response time at low driving voltage, which is attributed to the electron extraction barrier at the TiO₂/perovskite interface and the charge traps in the TiO₂ layer. Furthermore, the dark current of SnO₂-based perovskite photodiodes is effectively suppressed by inserting a poly(vinylpyrrolidone) interlayer, and then the on/off current ratio increases to 1.2×10^6 , corresponding to an improvement of 1 order of magnitude. Such low-cost, solution-processable perovskite photodetectors with high performance show promising potential for future optoelectronic applications.

KEYWORDS: perovskite, photodetectors, electron transport layer, response time, dark current



INTRODUCTION

Metal halide perovskites with an ABX₃ structure have attracted great attention as promising optoelectronic materials due to their unique optical and electronic properties, such as direct band gap with large absorption coefficient, ultrafast charge generation, high and microsecond-long balanced mobilities, and slow recombination.^{1,2} Especially in the photovoltaic field, rapid progress of perovskite solar cells has been witnessed by the rocketing power conversion efficiency (PCE) rising from 3.8 to 22.1% in the past few years.^{3,4} Besides solar cells, there have been some pioneering studies on fabricating perovskite-based photodetectors, revealing their excellent performances.^{5–18}

Generally, perovskite-based photodetectors can be classified into two types according to the device architecture: lateral structure (photoconductors) and vertical structure (photodiodes).^{18–20} Recently, perovskite photodetectors using a wide range of materials, including thin films, nanowires, microplates, and single crystals, have been reported.^{18–21} In most works, the lateral structure, which employs two identical coplanar electrodes on a perovskite layer, was adopted for its fabrication simplicity. The major limitation of photoconductor devices is their long response times. In a photodiode, photoexcited electron–hole pairs are separated by the inner electric fields,

which makes it operable at zero bias without consuming external power. Furthermore, the distance between the two electrodes can be easily reduced to hundreds of nanometers by controlling the thickness of the perovskite absorption layer. Thus, photodiodes have shorter response times and lower noise than photoconductors.^{18,19}

Similar to perovskite solar cells, perovskite photodiodes (PPDs) usually take a sandwich structure, in which a perovskite film is sandwiched between an electron transport layer (ETL) and a hole transport layer. For perovskite solar cells, developing new electron transport materials and modifying the interlayer have been demonstrated to be an effective approach to improve device efficiency and stability. It might be thought that the ETL could also be a crucial factor in determining the performance of PPDs. However, the effects of ETL on the performance of PPDs were rarely studied. In most works, the commonly used electron transport materials in perovskite solar cells, such as TiO₂, C₆₀, [6,6]-phenyl-C₆₁ butyric acid methyl ester (PCBM), and poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluo-

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rene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN), were directly used as ETLs in PPDs. Recently, adopting composite ETLs, such as PFN/PCBM,⁶ Al₂O₃/PCBM,⁷ PCBM/C₆₀,⁸ PCBM/TiO₂,²² and PCBM/poly(methyl methacrylate),²³ has shown, in many instances, enhancement of device performance. Using a conjugated polymer PFN as the hole-blocking layer on the top of PCBM ETL in an inverted-structure photodiode, Dou et al. reduced the dark current density and achieved a very high detectivity of 10¹⁴ Jones.⁶ Lin et al. utilized relatively thick PCBM/C₆₀ ETLs to manipulate the device electro-optics, from whence they achieved control over junction capacitance, dark current, and frequency response without compromising the linear dynamic range (LDR).⁸ As aforementioned, many studies have been reported on the suppression of dark current densities by modifying ETLs due to improving hole-blocking ability or passivating the interface defects. Nevertheless, there is no report on the influence of ETLs on the response time of PPDs. Further improvements in the performance of PPDs are also expected by designing and optimizing ETLs to achieve large responsivity, high specific detectivity, and short response time.

As mentioned previously, a series of efficient ETLs have been developed to improve the performances of perovskite solar cells. Among them, solution-based TiO₂ is the most commonly used electron transport material because it has specific energy level, resulting in excellent electron-transporting and hole-blocking characteristics. In addition to TiO₂, SnO₂ has been recently shown to be a more efficient electron transport material in perovskite solar cells.^{24–28} SnO₂ has a deeper conduction band and higher electron mobility compared to traditional TiO₂, which can enhance charge transfer from perovskite to electron transport layers.²⁸ In this study, we compared the performances of PPDs with different ETLs, especially on the response time. Two commonly used ETLs in perovskite solar cells, i.e., TiO₂ and SnO₂, were adopted for fabricating PPDs. Both PPDs exhibit a high on/off current ratio of 10⁵, a large detectivity around 10¹² Jones, and an LDR of over 80 dB. We found that the photodetectors with TiO₂ ETLs had low responsivity and long response time at low driving voltage, which is similar with the “light-soaking” effect in perovskite solar cells. The poor performance of TiO₂-based PPDs under low driving voltages is attributed to the presence of electron extraction barrier at the TiO₂/perovskite interface and the charge traps in the TiO₂ layer. Unlike the TiO₂-based devices, SnO₂-based PPDs show an ultrahigh response rate. Moreover, the dark current is effectively suppressed by inserting a poly(vinylpyrrolidone) (PVP) interlayer as an interfacial layer, and then the on/off current ratio increases to 1.2 × 10⁶, corresponding to an improvement of 1 order of magnitude.

RESULTS AND DISCUSSION

The device structure of perovskite photodetectors used in this work has the following architecture: indium tin oxide (ITO)/ETL (SnO₂ or TiO₂)/perovskite/2,2',7,7'-tetrakis(*N,N*-dimethoxyphenylamine)-9,9'-spirobifluorene (Spiro-MeOTAD)/Au, as schematically shown in Figure 1a. On top of the ITO-coated glass (as cathode), the SnO₂ or TiO₂ nanoparticle films were spin-coated and then low-temperature-annealed. The perovskite layer was prepared by the two-step method and sandwiched between the ETL and the spin-coated Spiro-MeOTAD layer. Finally, Au top electrodes (as anode) were thermally evaporated through a shadow mask. Figures 1b and S1 show the typical cross-sectional scanning electron microscopy (SEM) images of PPDs based on SnO₂ and TiO₂

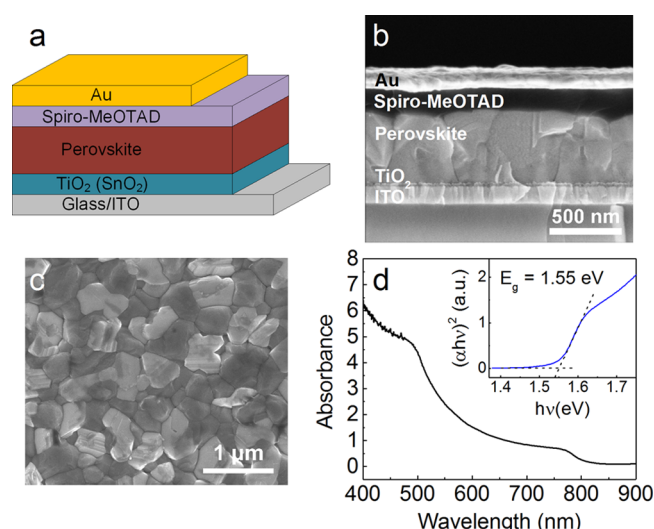


Figure 1. (a) Schematic diagram of the device structure of the perovskite photodetector. (b) Cross-sectional SEM image of the completed TiO₂-based PPD. (c) SEM image of the fabricated (FAPbI₃)_{1-x}(MAPbBr₃)_x film on top of the ITO/TiO₂ layer. (d) UV–visible (vis) absorption spectrum of the perovskite film on a quartz substrate (the inset shows optical band gap (1.55 eV) analysis of perovskite from (d)).

ETLs, respectively, and each of the component layers can be easily distinguished. The thicknesses of TiO₂, perovskite, Spiro-MeOTAD, and Au layer are 30, 500, 150, and 130 nm, respectively. X-ray diffraction (XRD) peaks for SnO₂ and TiO₂ nanoparticle films are indexable to the anatase TiO₂ structure and the tetragonal SnO₂ structure (Figure S2),²⁹ respectively, indicating the formation of pure TiO₂ and SnO₂ crystals. The average crystalline sizes of the nanoparticles were estimated by the Debye–Scherrer equation to be 2.5 nm for TiO₂ and 4.6 nm for SnO₂. The thicknesses of SnO₂ and TiO₂ layers have been optimized, and the ETLs should fully cover the ITO substrate, but they must not be so thick as to introduce a high series resistance.

It has been reported that a small amount of MAPbBr₃ added into FAPbI₃ is favorable for improving perovskite phase stabilization.³⁰ In this work, a mixture of perovskite layer (FAPbI₃)_{1-x}(MAPbBr₃)_x was selected, and the composition of MAPbBr₃ was about 3%. Figure 1c presents the surface morphology of the fabricated (FAPbI₃)_{1-x}(MAPbBr₃)_x film on top of the ITO/TiO₂ layer. The perovskite film shows a uniform and pinhole-free surface morphology as well as well-developed grains with sizes of a few hundred nanometers. In addition, some white particles were formed on the surface of the perovskite film, which was confirmed to be PbI₂ by the corresponding XRD pattern (Figure S3), due to partial decomposition of the FAPbI₃ layer during annealing.²⁸ Previous works indicated that PbI₂ could passivate the defects and reduce recombination, and the perovskite film with appropriate excess PbI₂ has been shown to improve device performance.^{28,31,32} The XRD (Figure S3) and SEM (Figure S4) results indicate that different substrates (TiO₂ and SnO₂) have little influence on the morphology and quality of perovskite layers. Moreover, the strong and broad absorption in the UV and visible-light ranges reveals that the (FAPbI₃)_{0.97}(MAPbBr₃)_{0.03} perovskite layer is a good light absorber, as shown in Figure 1d. A very sharp absorption edge is a strong indication for a direct band gap nature. Using the formula for a direct band

semiconductor,³³ the optical band gap of (FAPbI₃)_{0.97}(MAPbBr₃)_{0.03} is estimated to be 1.55 eV (inset of Figure 1d), which is consistent with the previously reported values.^{26,30,34}

Figure 2a shows the current density–voltage (*J*–*V*) curves of the SnO₂- and TiO₂-based PPDs measured in the dark and

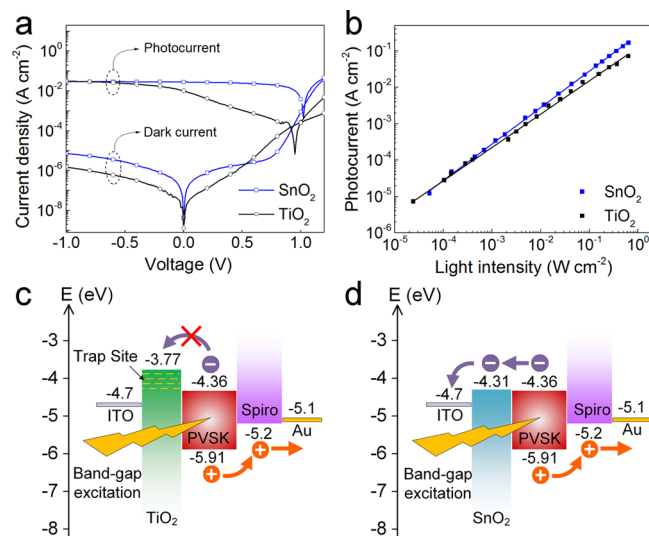


Figure 2. (a) *J*–*V* curves of the SnO₂- and TiO₂-based PPDs measured in the dark and under 450 nm laser irradiation with a light density of 100 mW cm⁻². (b) Linear dynamic range of TiO₂- and SnO₂-based PPDs. Energy band diagram at 0 V bias under illumination of (c) TiO₂-based and (d) SnO₂-based PPDs.

under 450 nm laser irradiation with a light density of 100 mW cm⁻². As extracted from Figure 2a, dark currents of the SnO₂- and TiO₂-based PPDs are 2.8×10^{-6} and 4.6×10^{-7} A cm⁻² under a reverse bias of -0.5 V, respectively. The slightly higher

dark current for the SnO₂-based PPD is attributed to the higher conductivity of SnO₂ than TiO₂ because the mobility of the SnO₂ film (1.9×10^{-3} cm² V⁻¹ s) is 2 orders of magnitude higher than that of TiO₂ (3.3×10^{-5} cm² V⁻¹ s).²⁸ The photocurrent keeps almost a constant value of ~ 30 mA cm⁻² when the reverse bias decreases from -1.0 to 0 V for the SnO₂-based PPD. In contrast to the SnO₂-based PPD, the TiO₂-based device exhibits bias-dependent photocurrent, which keeps at the same level as the SnO₂-based device under the larger reverse bias. Nevertheless, the photocurrent decreases obviously when the reverse bias is lower than -0.6 V. The different photocurrent–voltage characteristics lead to a distinct difference in the light on/off ratio. The on/off ratios were determined to be 4.1×10^3 and 2.0×10^4 under -1.0 V for the SnO₂- and TiO₂-based PPDs, respectively. At a low reverse bias of -0.05 V, the on/off ratio improves to the same level of 2.0×10^5 for both PPDs. As one of the most important parameters, the specific detectivity (*D*^{*}) characterizes how weak light it can detect. When the dark current is dominated by shot noise, *D*^{*} can be expressed as

$$D^* = \frac{J_{ph}/L_{light}}{(2qJ_d)^{1/2}} \quad (1)$$

where *J*_{ph} is the photocurrent, *L*_{light} is the incident light intensity, *J*_d is the dark current, and *q* is the elementary charge. The specific detectivity at 450 nm was then calculated to be about 1.2×10^{12} Jones (Jones = cm Hz^{1/2} W⁻¹) under -0.05 V for both PPDs. This value is comparable to the commercial Si photodiode at the same wavelength,³⁵ demonstrating its potential application in weak visible-light sensing. Another figure of merit of photodetectors is the LDR, which represents the light intensity range in which the responsivity of the photodetector keeps constant. Figure 2b shows that the photocurrent increases linearly with increasing light intensity

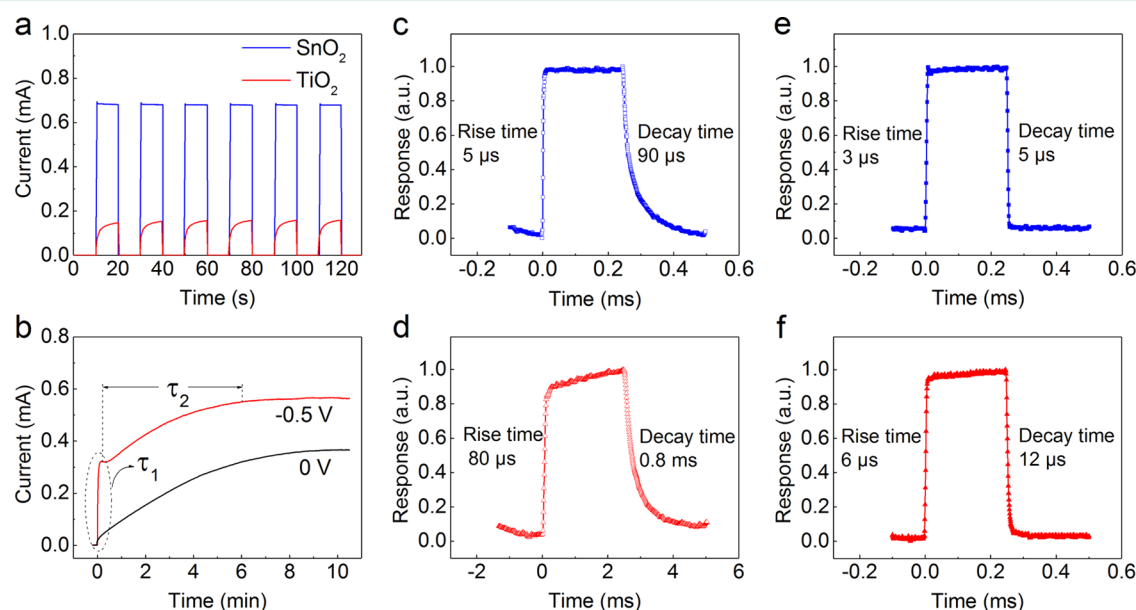


Figure 3. (a) *I*–*t* curves of the SnO₂- and TiO₂-based PPDs at 0 V bias under 450 nm irradiation with a light density of 60 mW cm⁻². (b) *I*–*t* curves of the TiO₂-based PPD under 450 nm laser irradiation at different bias voltages after a single switch-on operation. The rise time can be divided into two components. τ_1 is a transient response with a very short time constant, whereas τ_2 shows a time constant of around 6 min. (c–f) Normalized high-resolution photoresponse of the (c, e) SnO₂-based PPDs and (d, f) TiO₂-based PPDs at (c, d) 0 V and (e, f) -0.5 V reverse bias for rise and decay times.

across greater than 4 decades of laser intensity, corresponding to an LDR exceeding 80 dB.

The difference in photoresponse for the photodetectors with different ETLs can be understood from their energy band diagram at 0 V bias under illumination, as shown in Figure 2c,d, in which the data of energy band levels are taken from the previous works.^{6,28,36,37} In view of the line-up presented in Figure 2c,d, there appears to be an energy barrier of 0.59 eV between the conduction band minimum (CBM) of (FAPbI₃)_{0.97}(MAPbBr₃)_{0.03} and TiO₂, whereas there is almost no barrier in the SnO₂/perovskite case. Thus, photogenerated electrons hardly move from the perovskite layer to the ITO through the barrier in the TiO₂-based PPDs, leading to lower photocurrents at the lower reverse bias. When the reverse bias is higher than the energy barrier of 0.59 V, the driving force imposed onto the photogenerated electrons is enough to overcome the energy barrier between TiO₂ and perovskite, thereby resulting in an almost same photocurrent as the SnO₂-based device.

To explore the response characteristics, the current–time (*I*–*t*) curves were measured at 0 V bias under 450 nm laser irradiation with a light density of 60 mW cm^{−2} for both PPDs, as shown in Figure 3a. The current in the dark and under illumination was controlled by a light shutter. The photocurrent of the SnO₂-based PPD is higher than that of the TiO₂-based device, which is consistent with the results in Figure 2a. The on/off switching behavior for both PPDs is preserved over multiple cycles, indicating the robustness and reproducibility of both photodetectors. In notable contrast, however, the photocurrent sharply increases for the SnO₂-based PPD after the laser is turned on, whereas it slowly rises with time for the TiO₂-based device. Similar temporal photoresponse characteristics were also observed for both PPDs under −0.5 V reverse bias (Figure S5). To further explore the temporal photoresponse, the *I*–*t* curves of the TiO₂- and SnO₂-based PPDs were measured under 450 nm laser irradiation after a single switch-on operation, as shown in Figures 3b and S6, respectively. Obviously, the rise time of the TiO₂-based PPD can be divided into two components. The first component (τ_1) is a transient response with a very short time constant, whereas the second component (τ_2) shows a time constant of around 6 min. Unlike the TiO₂-based PPDs, the SnO₂-based detectors exhibit a transient response without the slow component (Figure S6). The phenomenon of double-exponential rise indicates the existence of two mechanisms, probably related to intrinsic photoresponse and light-soaking effect, which will be discussed in detailed later.

To obtain a precise value of τ_1 , the *I*–*t* curves of the device were measured using a 450 nm continuous laser, which was switched on and off by a chopper. The rise time and decay time are defined as the time rise to 90% of the maximum photocurrent from the dark current and recovery to 10% of the maximum photocurrent, respectively. As shown in Figure 3c, the rise time and decay time of the SnO₂-based photodetector at 0 V are determined to be 5 and 90 μ s, respectively. In contrast, the on/off switching of the TiO₂-based PPDs at 0 V is obviously slower than that of the SnO₂-based device, and it shows an 80 μ s rise time and a 0.8 ms decay time (Figure 3d). The higher response speed for the SnO₂-based device is attributed to a better match of energy level between SnO₂ and perovskite. The rise time depends on the collection of photogenerated carriers, and electrons in the perovskite layer can be efficiently transported to the SnO₂ layer because the

CBM of SnO₂ is very close to that of perovskite. On the contrary, electrons hardly move from the perovskite layer to TiO₂ because of an energy barrier of 0.59 eV. Thus, the rise time of the SnO₂-based detector is shorter than that of the TiO₂-based device. Furthermore, in all devices, the decay time is shorter than the rise time, indicating the slow recombination of holes and electrons in the perovskite layer. It is known that the photocurrent decay time of detector is related to the carrier recombination time. As shown in Figure 2c, for both devices, holes can be efficiently and rapidly transported to the Au anode because of the lower valence band maximum of Spiro-MeOTAD compared to the perovskite. However, there appears to be a small energy barrier of 0.05 eV between the CBM of SnO₂ and perovskite, the electron and hole fluxes cannot be balanced, and the electrons are accumulated at traps in the SnO₂/perovskite layer under 0 V bias. Consequently, the recombination of the photogenerated electron–hole pairs in the perovskite layer is reduced, resulting in increased carrier lifetime. This effect (i.e., accumulation of photogenerated electrons at the TiO₂/perovskite interface) is more dominant for the TiO₂-based device because of the much higher energy barrier of 0.59 eV. As a result, the decay process becomes limited by the poor recombination cross section.

When the PPDs are operated under a reverse bias of −0.5 V, both rise and decay times are significantly reduced (Figure 3e,f). The extracted rise and decay times are 3 and 6 μ s for the SnO₂-based PPD at −0.5 V, respectively, which are comparable to the best reported values for perovskite photodetectors.^{7,8} In addition, unlike at 0 V bias, the rise time and decay time (6 and 12 μ s, respectively) of the TiO₂-based PPD are closer than those of the SnO₂-based device (3 and 5 μ s, respectively). In the presence of reverse bias, the driving force imposed onto the photogenerated electrons is enough to overcome the energy barrier between ETL and perovskite. Therefore, both electrons and holes can be efficiently and rapidly extracted to respective electrodes and the decay time is close to the rise time for both PPDs.

The temporal photoresponse of PPDs was also investigated under forward bias to investigate the origin of long component rise time. When the device is biased at zero bias or forward bias, it is in photovoltaic mode and operated as a solar cell. The *J*–*V* curves of the TiO₂-based PPD with different light-irradiation times are shown in Figure 4a. The TiO₂-based device exhibits S-shaped *J*–*V* curves in the initial illumination with lower PCE and fill factor. With increasing irradiation time, the device metrics gradually recover and finally reach a saturated state after 8 min irradiation. This process was previously known as the “light-soaking” issue in polymer and perovskite solar cells.^{38–41} By contrast, the SnO₂-based detector has reproducible and stable *J*–*V* characteristics during the initial *J*–*V* sweep and upon different irradiation times (Figure S7), demonstrating the absence of a light-soaking problem. Trap-filling in TiO₂ by photogenerated charges, leading to an increased conductivity of the TiO₂ layer, has been proposed to be the underlying reason.^{38,39} One way to overcome the light-soaking problem is to chemically dope TiO₂ with other elements, which can significantly reduce its work function. Furthermore, the light-soaking effects are more negative for photodetectors than for solar cells because solar cells usually work under steady-state illumination, whereas a fast response for illumination is required for most photodetectors.

To reveal the possible effects of ETLs on the photoresponse of devices, the *I*–*V* characteristics of both TiO₂ and SnO₂ thin

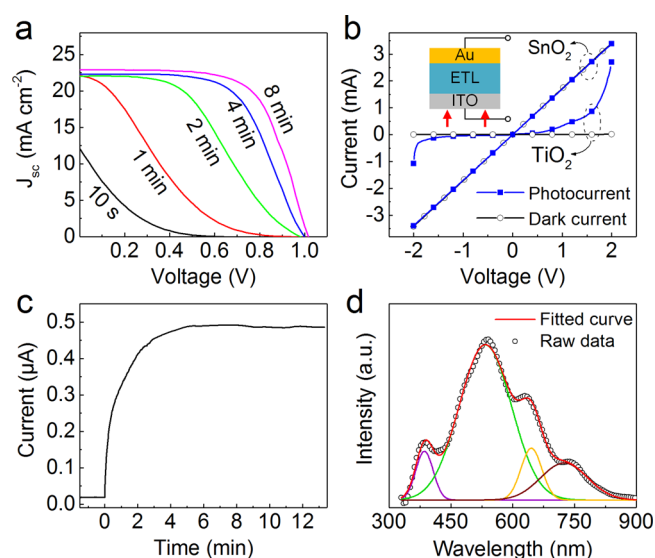


Figure 4. (a) J - V curves of the TiO_2 -based PPD operated as a solar cell under a simulated AM1.5G spectrum with different light-irradiation times. (b) I - V characteristics of TiO_2 and SnO_2 thin films with device structure of ITO/metal oxides/Au with and without 450 nm laser illumination. The inset shows the device structure. (c) Temporal photocurrent response of the TiO_2 film under 450 nm laser illumination. (d) Photoluminescence (PL) spectrum of the TiO_2 film at room temperature and its four Gaussian fit peaks.

films with device structure of ITO/metal oxides/Au were measured with and without light illumination, as shown in Figure 4b. The dark current of the SnO_2 film is much higher than that of the TiO_2 film, confirming the higher conductivity of the SnO_2 layer. More importantly, the photocurrent of the SnO_2 film is very close to its dark current, whereas the TiO_2 film shows a drastic increase in current after light illumination. This result implies the presence of a photoconductivity effect in the TiO_2 film. To further evaluate the photoconductivity effect, Figure 4c shows the temporal photocurrent response of the TiO_2 film. Upon light illumination, the photocurrent exponentially increases with irradiation time with a time constant of ~ 4 min, which is very close to the long component rise time τ_2 and the light-soaking time for the TiO_2 -based PPDs, implying the same mechanism. Therefore, we propose that the long component rise time for the TiO_2 -based detector, as well as the light-soaking effect, is attributed to the photoconductivity effect of the TiO_2 layer.

To fully reveal the underlying mechanism of long component rise time, we measured the photoluminescence (PL) spectrum of TiO_2 film at room temperature. The original PL spectrum of TiO_2 and its four Gaussian fitting peaks are illustrated in Figure 4d. The 386 nm peak is originated from the transition of electrons from the conduction band to the valence band, according to the electronic structure of anatase (3.2 eV). The broad peak at 534 nm is associated with the oxygen vacancies losing one electron (F^+ center).^{42,43} The PL peaks at 645 and 724 nm are related to the formation of Ti^{3+} ions and the associated defect states.⁴⁴ The defect-related emission in the visible region is very strong compared to the UV emission, inferring the high defect density inside the TiO_2 film. We propose that the presence of a large number of defects in TiO_2 is responsible for the long component rise time τ_2 (as well as the light-soaking effect) observed in the TiO_2 -based detector. As demonstrated in Figure 4c, the conductivity of TiO_2 is sensitive to light exposure because illumination can lead to the direct excitation of electrons from the valence band to the conduction band (or from the valence band to the conduction band via the defect states). Upon light illumination, the initially excited electrons must fill the defect states that are present in the forbidden band of TiO_2 and then the photoconductivity increased gradually under continuous illumination and saturated when all of the defect states are filled. Increasing photoconductivity of TiO_2 reduces the serial resistance of the TiO_2 -based PPDs, resulting in the observed long component rise time τ_2 .

The above results suggest that the performance of SnO_2 -based PPDs is better than that of TiO_2 -based devices owing to a better match of energy level between SnO_2 and perovskite compared to TiO_2 . However, the dark current of SnO_2 -based PPD is relatively high due to the higher conductivity of the SnO_2 layer. Previous works have demonstrated that the dark current of PPDs could be significantly suppressed by adding an interlayer or through interfacial engineering.^{6–8,22} In this work, a thin poly(vinylpyrrolidone) (PVP) interlayer, which has a larger optical band gap than SnO_2 , was inserted between SnO_2 ETL and perovskite layer to suppress the dark current. The thickness of the PVP layer varied from 2.1 to 7.8 nm by controlling the concentration of the precursor solution (Figure S8). As demonstrated in Figures S3 and S4, the thin PVP interlayer has little effect on the morphology and quality of the subsequent perovskite layer. The optimum thickness of the PVP interlayer was determined to be ~ 3.2 nm (Figure S9). Figure 5a shows the dark current and photocurrent density curves (under 450 nm laser irradiation with a light density of

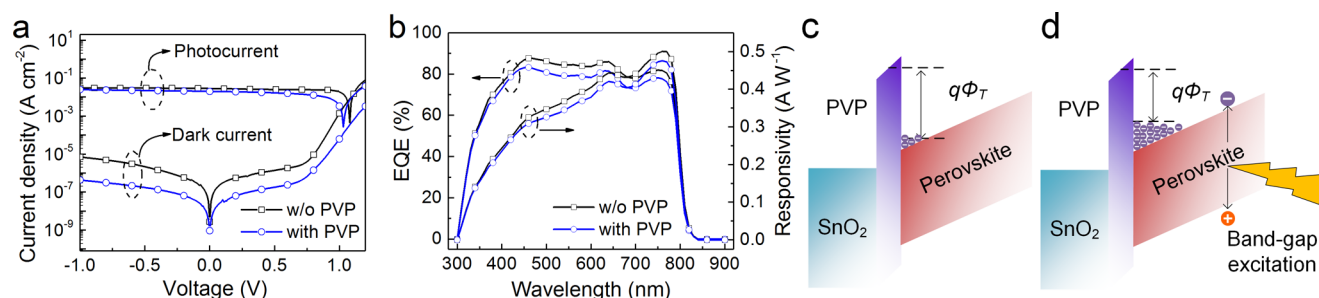


Figure 5. (a) Dark current and photocurrent density curves (under 450 nm laser irradiation with a light density of 100 mW cm^{-2}) of the SnO_2 -based PPDs with and without a 3.2 nm PVP interlayer. (b) EQE spectra and spectral responsivity (R_λ) of the SnO_2 -based PPDs with and without a 3.2 nm PVP interlayer. (c, d) Schematic energy band diagram of the SnO_2 -based PPD with a thin PVP interlayer (c) in dark and (d) under light illumination.

100 mW/cm²) of the SnO₂-based PPD with and without a 3.2 nm PVP interlayer under the bias ranging from −1.0 to 1.2 V, respectively. As extracted from Figure 5a, after introducing the PVP interlayer, the dark current greatly reduces from 1.6×10^{-7} to 1.8×10^{-8} A cm^{−2} under a reverse bias of −0.05 V, whereas the photocurrent is only slightly decreased from 28.5 to 20.2 mA cm^{−2}. Then, the light on/off ratios were determined to be 1.2×10^6 and 1.8×10^5 for the SnO₂-based PPDs with and without the PVP interlayer, respectively. Notably, by introducing the PVP interlayer, the on/off ratio is enhanced by approximately 1 order of magnitude. The external quantum efficiency (EQE) and spectral responsivity (R_λ) of the photodetector with and without PVP interlayer at different wavelengths are shown in Figure 5b, respectively. Both devices exhibit high EQEs (75–85%) in the wavelength range of 400–760 nm and hence they are suitable for visible-light broad-band photodetection. After adding the PVP interlayer, both EQE and R_λ drop little, which is consistent with the slight reduction of photocurrent for the device with PVP layer. Besides, the photoswitching behavior (Figure S10) and the LDR (Figure S11) of the SnO₂-based PPD with the PVP interlayer show similar features compared to its counterpart without the PVP interlayer.

These results demonstrate that the PVP interlayer can effectively suppress the dark current of perovskite photodetectors and that it has little effect on the other device performance, which can be understood on the basis of the energy diagram shown in Figure 5c,d. When the PVP insulator layer is thin, the carrier transport from the perovskite film to the SnO₂ layer is controlled by direct tunneling. The introduction of PVP interlayer will incur an additional tunneling probability factor for the device current, which can be described by eq 2⁴⁵

$$J \propto T_t \approx \exp(-\alpha_T d \sqrt{q\phi_T}) \quad (2)$$

where $\alpha_T = 2\sqrt{2mqm^*}/\hbar$ approaches unity if the effective mass in the insulator equals the free electron mass, d is the thickness of PVP layer, q is the elementary charge, and ϕ_T is the tunnel barrier height. It is obvious that after inserting the PVP interlayer the additional tunneling probability factor T_t will significantly reduce the dark current density because of the higher ϕ_T . Upon illumination, with a photoenergy larger than that of the semiconductor band gap, the perovskite film absorbs photons to generate a large number of electron–hole pairs. These photogenerated electrons give rise to an increase in electron-filling level in the conduction band of perovskite, resulting in a reduction of the tunnel barrier height ϕ_T , as shown in Figure 5d. As the tunnel barrier height decreases, the tunneling probability factor T_t increases and consequently the photocurrent recovers its initial level of the counterpart without the PVP interlayer. In other words, the increased carrier density in the perovskite film upon illumination lowers the effective barrier height, leading to the easier carrier tunneling and transport and thus to an amelioration of negative effect of the PVP interlayer in the photocurrent.

CONCLUSIONS

In summary, the PPDs based on SnO₂ and TiO₂ ETLs were fabricated via a facile and low-cost solution-processing strategy and their performances were compared. Both PPDs exhibit a high on/off current ratio of 10^5 , a large detectivity of more than 10^{12} Jones, and a linear dynamic range of over 80 dB. Because

of the electron extraction barrier at the TiO₂/perovskite interface and charge traps in the TiO₂ layer, the TiO₂-based PPDs exhibit worse performance under low driving voltage, such as a low responsivity and a long response time. Especially, the temporal response of TiO₂-based PPDs indicates two different decay times on the order of 80 μ s and 0.8 ms at 0 V and the photoconductivity effect of the TiO₂ layer is responsible for the observed long component rise time. Furthermore, the SnO₂-based PPDs show an ultrahigh response rate of 3 μ s for the rise and 6 μ s for the decay times at −0.5 V. The dark current of SnO₂-based PPDs is suppressed effectively by introducing a PVP interlayer, and the on/off current ratio is increased by 1 order of magnitude, whereas the other device performance keeps almost unchanged. This work inspires the development of cheap and high-performance perovskite-based photodetectors.

EXPERIMENTAL SECTION

Materials. SnO₂ colloid precursor was purchased from Alfa Aesar (tin(IV) oxide, 15% in H₂O colloidal dispersion). TiO₂ nanoparticles were prepared by the method mentioned in ref 28. The final TiO₂ nanoparticles were dispersed in ethanol to make a suspension with a concentration of 6 mg mL^{−1}. TiAcAc was added into the solution with a final concentration of 15 μ L mL^{−1} to stabilize the as-obtained TiO₂ solutions. Lead iodide (PbI₂) was dissolved in dimethylformamide with a concentration of 1.3 mol mL^{−1}. The mixture solutions of FAI/MABr/MACl were prepared by dissolution of HC(NH₂)₂I, CH₃NH₃Br, and CH₃NH₃Cl (60:6:6 by weight in milligrams) in 1 mL isopropyl alcohol. The Spiro-OMeTAD solution was prepared by dissolving 72.3 mg of 2,2',7,7'-tetrakis(*N,N'*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene in 1 mL of chlorobenzene with 30 μ L of 4-*tert*-butylpyridine and 35 μ L of Li-bis(trifluoromethanesulfonyl)imide (170 mg mL^{−1} in acetonitrile).

Device Fabrication. The glass/ITO substrate with a sheet resistance of 15 Ω sq^{−1} was sequentially washed with detergent, distilled water, acetone, and isopropyl alcohol. After drying with nitrogen, the cleaned ITO substrates were treated with UV ozone for 10 min. For SnO₂ films, the ITO substrate was spin-coated with a thin layer of SnO₂ nanoparticle (diluted to 5%) at 4000 rpm for 30 s and annealed in ambient air at 180 °C for 30 min. For TiO₂ films, 6 mg mL^{−1} TiO₂ solution was spin-coated on ITO substrates at 2000 rpm for 30 s and annealed in ambient air at 150 °C for 30 min. After depositing the ETL, the perovskite layer was deposited in a glovebox by a two-step spin-coating method. First, 1.3 M PbI₂ solution was spin-coated onto the SnO₂ or TiO₂ ETL at 2500 rpm for 30 s and then annealed at 70 °C for 15 min. After the PbI₂ had cooled to room temperature, the mixture solution of FAI/MABr/MACl was spin-coated onto the PbI₂ layer at 2500 rpm for 30 s and then thermally annealed at 150 °C for 15 min under ambient condition. Next, the Spiro-OMeTAD solution was spin-coated at 2500 rpm for 30 s. Finally, the Au electrode (100 nm) was deposited on the Spiro-OMeTAD layer at a rate of 4 \AA s^{−1} via thermal evaporation using a shadow mask. For PVP interface-modified devices, after spin-coating SnO₂ films, 0.5 wt % PVP solution in dimethyl sulfoxide was spin-coated onto the SnO₂ layer at 2000 rpm for 1 min and then annealed at 150 °C for 15 min to induce cross-linking.

Characterization. Field emission scanning electron microscopy (FEI Nova Nano SEM-650) was used to acquire SEM images, with an electron beam accelerated at 500 V to 30 kV. X-ray diffraction (XRD) measurements were carried out using a Rigaku D/MAX-2500 diffractometer with a Cu K α X-ray source. PL spectra of TiO₂ thin films on Si substrate were measured with a Raman spectrometer (Horiba Jobin Yvon LabRam HR800) at room temperature, using a continuous beam of He–Cd laser of 325 nm wavelength as the excitation source. The optical absorption spectra of the samples were acquired using a Varian Cary 5000 UV–vis spectrophotometer in double-beam mode. The PVP film thickness was measured by an ellipsometer. All of the device measurements were performed under

ambient conditions. The I – V characteristics were acquired using a Keithley 2450 source meter in the dark and under illumination. A diode laser with wavelength of 450 nm was utilized as the light source, and the output power was measured using a laser power meter. The temporal photocurrent response was measured by a Tektronix TDS2012B Digital Storage Oscilloscope. The on–off illumination was switched by a mechanical chopper, and the frequency was 200 or 2000 Hz. When the PPDs were operated in solar cell mode, the J – V curves were taken using a Keithley 2400 source measurement unit under a simulated AM1.5G spectrum. The EQE spectra were recorded with an Enli Tech (Taiwan) EQE measurement system.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b18511.

SEM images, XRD patterns, UV–visible absorption spectra, and photodetector results (PDF)

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Notes

The authors declare no competing financial interest.

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