# **PHOTONICS** Research



# Environment-friendly antisolvent tert-amyl alcohol modified hybrid perovskite photodetector with high responsivity

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Received 2 December 2020; revised 14 January 2021; accepted 20 January 2021; posted 2 March 2021 (Doc. ID 416580); published 28 April 2021

The preparation of high-quality perovskite films with optimal morphologies is important for achieving high-performance perovskite photodetectors (PPDs). An effective strategy to optimize the morphologies is to add antisolvents during the spin-coating steps. In this work, a novel environment-friendly antisolvent tert-amyl alcohol (TAA) is employed first to improve the quality of perovskite films, which can effectively regulate the formation of an intermediate phase staged in between a liquid precursor phase and a solid perovskite phase due to its moderate polarity and further promote the homogeneous nucleation and crystal growth, thus leading to the formation of high-quality perovskite films and enhanced photodetector performance. As a result, the responsivity of the PPD reaches 1.56 A/W under the illumination of 532 nm laser with the power density of  $6.37 \ \mu\text{W/cm}^2$  at a bias voltage of  $-2 \ \text{V}$ , which is good responsivity for PPDs with the vertical structure and only CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite as the photosensitive material. The corresponding detectivity reaches  $1.47 \times 10^{12}$  Jones, while the linear dynamic range reaches 110 dB. These results demonstrate that our developed green antisolvent TAA has remarkable advantages for the fabrication of high-performance PPDs and can provide a reference for similar research work. © 2021 Chinese Laser Press

https://doi.org/10.1364/PRJ.416580

# **1. INTRODUCTION**

Photodetectors (PDs) that can convert hard-to-quantify optical signals into electrical ones that can be accurately detected are of great importance for a lot of industrial and scientific applications such as imaging, optical communications, chemical/biological sensing, and environmental monitoring [1–6]. For PDs, the most critical is the semiconductor material, which is used to absorb the incident photons and generate effective carriers (electrons and holes) upon photo-excitation. Then, the separated electrons and holes are transferred to the cathode and anode under the action of a built-in or applied electric field to produce an electric current [7]. At present, commercially available PDs mainly use inorganic semiconductor materials, such as GaN, Si, and InGaAs [8-11]. PDs using such materials have the advantages of a mature and reliable preparation process and a clear working mechanism, but the disadvantages are that the preparation process is complex and expensive [12], coupled with mechanical inflexibility and high driving voltage [13],

which greatly limit their application scope. In the past few years, low-cost, solution-processable optoelectronic materials, such as organic materials, nanomaterials, and nanocomposites have shown great application potential in the preparation of flexible and large-area PDs [14-20], but shortcomings that cannot be ignored greatly hindered their broader applications and further development of the devices based on these materials, such as the low carrier mobility. Recently, perovskite materials have been widely used in solar cells [21-24], LEDs [25,26], lasers [27], and PDs [28,29] because of their unique characteristics, such as high carrier mobility, high optical absorption coefficient, long carrier diffusion length, and adjustable direct bandgap [30-32]. Perovskite PDs (PPDs) are suitable for visible light communication and imaging applications with a vertical structure because of the advantages of short carrier transmission distance, fast frequency response, and linear correlation between photocurrent and incident light intensity. Liu et al. and Sutherland et al. fabricated vertical PDs with CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (MAPbI<sub>3</sub>) as the photosensitive layer material

and obtained less-than-ideal responsivities of 0.34 A/W and 0.4 A/W under monochromatic illumination at wavelengths of 500 and 600 nm, respectively. The reasons for the unsatisfactory performance of PDs were greatly attributed to the poor morphologies of perovskite films and the defects existing on the grain boundaries and film surface. Therefore, it is important for improving the performance of PPDs to construct high-quality films with larger grain sizes, fewer grain boundaries, better crystallinity, and uniform morphologies. In order to better control the morphologies of the films, an effective method is to add antisolvents in the process of perovskite spin-coating, such as toluene, chlorobenzene, ethyl acetate, or mixed antisolvents, to regulate the formation of perovskite crystal nucleus and crystal grains growth, so as to obtain uniform and dense perovskite films without pinholes.

In this work, tert-amyl alcohol (TAA) as a novel green antisolvent was first employed to prepare high-quality perovskite films with a smooth and mirror-like surface, which greatly improved the performance of the PPDs. Through this method, the responsivity of the PDs reached 1.56 A/W under the illumination of 532 nm laser with a power density of  $6.37 \ \mu\text{W/cm}^2$  at a bias voltage of -2 V, which is a good responsivity we have known for PPDs with the vertical structure of glass/ITO/PEDOT:PSS/perovskite/PC61BM/BCP/Ag and only MAPbI<sub>3</sub> perovskite as the photosensitive material. The corresponding detectivity reached  $1.47 \times 10^{12}$  Jones, while the LDR reached 110 dB. In addition, we prepared PDs using isopropanol (IPA) and n-butanol (nBA) with polarity greater than TAA and toluene (TL) and chlorobenzene (CB) with polarity less than TAA as antisolvents for comparison. Judging from the obtained results, the PDs with TAA as the antisolvent had the best performance. We supposed that these results should be attributed to the better modification-assisted selectivity characteristics of TAA with moderate polarity than that of the other antisolvents, which would effectively regulate the formation of an MAIPbI2 · DMSO intermediate phase staged in between a liquid precursor phase and a solid perovskite phase and further promote the homogeneous nucleation and crystal growth in the subsequent annealing process, thus leading to the formation of high-quality perovskite films and enhanced PD performance. Moreover, it is worth noting that TAA is a green and environment-friendly antisolvent material. Compared with TL, CB, and other high-risk antisolvents, it has the advantages of low toxicity, low cost, and easy availability. These results provide a reference for the preparation of high-performance and environment-friendly PPDs in the future.

# 2. EXPERIMENTAL SECTION

# A. Materials Preparation

Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), lead iodide (PbI<sub>2</sub>, >99.99%), methylammonium iodide (CH<sub>3</sub>NH<sub>3</sub>I, MAI, >99.5%), phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM, >99%), and bathocuproine (BCP, >99%) were all purchased from Xi'an Polymer Light Technology Corp., Ltd. N,N-dimethylformamide (DMF, 99.5%), dimethylsulfoxide (DMSO, 99.5%), and tert-amyl alcohol (TAA) were all purchased from Aladdin.

#### **B.** Device Fabrication

The prepatterned glass/ITO was first cleaned ultrasonically in the order of glass cleaner, deionized water, acetone, and isopropanol; then, the ITO glass was treated with UV-ozone for 15 min to enhance its wettability. The MAPbI<sub>3</sub> perovskite solution was prepared by dissolving PbI2 and CH3NH3I with a molar ratio of 1:1.05 in a mixed-solvent system with DMF and DMSO at a volume ratio of 9:1. A 100 µL perovskite precursor solution was spin-coated on the ITO/PEDOT:PSS substrate at 6000 r/min for 30 s, and 250 µL TAA was slowly dropped on the wet film at about one tenth of a second during the spin-coating process; then, the film was briefly annealed at 100°C for 15 s, while the film turned black. All the spin-coating processes mentioned above were carried out in a glove box filled with nitrogen. Next, the samples were annealed in ambient air at 100°C for 15 min and then annealed at DMSO atmosphere at 100°C for 10 min. Subsequently, the chlorobenzene solution of PC<sub>61</sub>BM (20 mg/mL) and ethanol solution of BCP (0.7 mg/ mL) were successively spin-coated on the perovskite film. Finally, 100 nm thick silver was evaporated as the electrode.

## **C.** Characterization and Measurement

The cross-sectional images and surface morphologies of the different perovskite films were characterized using scanning electron microscopy (SEM, HITACHI SU 8020, Japan) and atomic force microscopy (AFM, CSPM5500, China). The cross-sectional EDS mapping images of different elements for each layer were characterized by a Talos F200X (FEI, The absorption of different antisolvent-America). processed perovskite films was measured by a Shimadzu UV-2600, Japan. The X-ray diffraction (XRD) measurement of perovskite films was performed by a D/MAX-2500, Japan. The steady-state and time-resolved photoluminescence spectra were recorded by a fluorescence spectrum (FLS 1000, Edinburgh Instruments, Britain). The Fourier transform infrared spectrum was recorded using the Nicolet iN10-FTIR microscope (Thermo Scientific, America). The I-V characteristics of all PDs under 405, 532, and 808 nm lasers illumination were measured using a Keithley 2400 source meter instrument.

# 3. RESULTS AND DISCUSSION

The architectural schematic of the PDs mentioned in this article is shown as Fig. 1(a), where indium tin oxide (ITO) acts as the anode electrode, and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and phenyl-C<sub>61</sub>-butyric acid methyl ester/bathocuproine (PC<sub>61</sub>BM/BCP) bilayer act as hole transport layer and electron transport layer, respectively. An organometal trihalide MAPbI<sub>3</sub> layer is sandwiched between the PEDOT:PSS and PC<sub>61</sub>BM layers as the light-absorbing material. On the top of the structure is silver (Ag) as the cathode electrode. Figure 1(b) displays the cross-sectional SEM images of each layer corresponding to the device in Fig. 1(a). Every layer of the PD is clearly observed in the SEM image, and the large grains throughout the active layer shown in the SEM image are attributed to the antisolvent-assisted crystallization with the participation of TAA. At the same time, we characterized the cross-sectional EDS mapping images of different elements

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Fig. 1. (a) Device architecture of PDs. (b) Cross-sectional SEM image of each layer in the device with a structure of (a). (c), (d) Crosssectional EDS mapping images of different elements for each layer of the device in (a). (e) Schematic processing scheme of the antisolventassisted perovskite deposition process; the dashed parts are the chemical structures of antisolvents used in this work (TAA, TL, CB, nBA, and IPA).

for each layer, as shown in Figs. 1(c) and 1(d). Figure 1(e) illustrates the schematic processing scheme of the antisolventassisted perovskite deposition process. In the spin-coating step, an intermediate phase staged in between a liquid precursor phase and a solid perovskite phase is formed rapidly with the participation of an antisolvent, and the main component of the intermediate phase is an MAI · PbI2 · DMSO adduct due to the interaction between Lewis base DMSO and/or iodide (I<sup>-</sup>) and Lewis acid PbI<sub>2</sub> [33], which will effectively facilitate the crystal growth and thus lead to the formation of large grains, as long as the intermediate phase is pure enough. The lower polarity TL and CB can rapidly facilitate the formation of crystal nucleus and, consequently, provide a supersaturated driving force for the formation of perovskite films [34]. However, due to the solubility difference of DMF and DMSO, the residual DMSO in the intermediate phase could not be effectively removed, resulting in uncontrolled nucleation and disordered crystallization in the film formation process of perovskite. Meanwhile, because of the slightly higher polarities of nBA and IPA (they are miscible with both DMF and DMSO), such unwanted miscibility might accelerate the saturation of the precursor solution and avoid formation of the intermediate phase through the more complete removal of the DMF and DMSO, resulting in smaller perovskite crystal grains (denoted as immature grains) and forming more inhomogeneous films [35]. TAA with moderate polarity has better modification-assisted



After annealing

Fig. 2. (a) Photograph of TAA-PSK film on ITO glass before annealing. (b) FTIR spectra of TAA-PSK films with and without annealing. (c) Photographs of different antisolvents processed films after annealing.

selectivity characteristics, which can effectively remove excessive DMF and DMSO without changing the stoichiometric ratio of the intermediate phase and further promote the homogeneous nucleation and crystal growth in the subsequent annealing process functioning as polar auxiliary sites, thus leading to the formation of high-quality perovskite films with smoother morphologies. Figure 2(a) shows the fresh TAA processed perovskite (TAA-PSK) film before annealing. The yellowish-brown film is indicative of the adduct of PbI<sub>2</sub> with Lewis base DMSO and iodide in MAI [33]. Figure 2(b) plots the corresponding Fourier transform infrared (FTIR) spectra of TAA-PSK films with and without annealing. The vibration peaks at 3186 cm<sup>-1</sup> and 1018 cm<sup>-1</sup> can be attributed to the N-H and S=O stretching vibration, respectively [36,37]. These two peaks belonging to perovskite and DMSO component demonstrate the existence of the intermediate phase. The photographs of different antisolvent-processed films after annealing at 100°C for 15 s in a glove box and at 100°C for 15 min in ambient air are displayed in Fig. 2(c); further, the energy band and charge transfer diagram of PDs mentioned in this work are plotted in Fig. 3.

The absorption spectra of the MAPbI3 perovskite films processed by different antisolvents are depicted in Fig. 4(a). All of the MAPbI<sub>3</sub> films show strong broadband absorption in the ultraviolet (UV) visible range with the absorption cut-off edge located at ~300 and ~800 nm, respectively. Moreover, a significantly enhanced absorbance is observed from



Fig. 3. Energy band and charge transfer diagram of PDs.



**Fig. 4.** Optical properties of different antisolvent-processed films. (a) Absorption spectra. (b) XRD patterns. (c) Steady-state PL spectra; inset plots the corresponding emission peak position. (d) TRPL spectra; inset plots the values of  $\tau_1$  and  $\tau_2$ .

the TAA-PSK film (red line) in comparison with TL processed perovskite (TL-PSK) film (green line), CB processed perovskite (CB-PSK) film (blue line), nBA processed perovskite (nBA-PSK) film (purple line), and IPA processed perovskite (IPA-PSK) film (orange line) in the optical absorption range of 325-600 nm, which implies that a higher photocurrent would be generated in the PPDs with TAA as the antisolvent. Figure 4(b) displays the X-ray diffraction (XRD) patterns of MAPbI<sub>3</sub> perovskite films spin-coated on the PEDOT:PSS substrate with the treatment of different antisolvents, where the typical strong diffraction peaks of the MAPbI3 films are located at 14.12°, 28.44°, and 31.88°, which can be well assigned to the (110), (220), and (310) crystal planes and indicate good crystallinity of the MAPbI<sub>3</sub> films. The steady-state photoluminescence (PL) spectra and time-resolved photoluminescence (TRPL) spectra are an important way to characterize the film quantity and relative nonradiative losses of charge carriers; further, the films discussed in this work were all spin-coated on the bare glasses. As shown in Fig. 4(c), the PL peaks of different perovskite films are located at 778.5 nm (TAA-PSK), 782.3 nm (TL-PSK), 782.3 nm (CB-PSK), 784.1 nm (nBA-PSK), and 786.0 nm (IPA-PSK), respectively. There is a slight blueshift of TAA-PSK film compared with the TL-PSK (3.8 nm), CB-PSK (3.8 nm), nBA-PSK (5.6 nm), and IPA-PSK (7.5 nm) films. Moreover, the PL intensity of TAA-PSK film is higher than that of the other four antisolvent-processed films. It is well known that the better-quality perovskite films with larger grain sizes and fewer electronic defects result in the blueshift of PL peaks, and the higher PL intensity indicates the less nonradiative recombination of charge carriers [38,39]. The above data show that the TAA-PSK film has the best morphology and crystallinity. The result is also confirmed by TRPL decay curves in Fig. 4(d), and the carrier lifetime values were obtained by using the biexponential decay function

$$Y = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2),$$
 (1)

where  $\tau_1$  and  $\tau_2$  denote the fast and slow decay times. As seen in Table 1, the PL lifetimes ( $\tau_2$ ) of TL-PSK, CB-PSK, nBA-PSK,

Table 1. Summary of the Performance of PDs

Samples	$ au_1$ (ns)	A <sub>1</sub> (%)	$ au_2$ (ns)	A <sub>2</sub> (%)
TAA-PSK	20.68	27.68	80.82	72.32
TL-PSK	2.43	37.96	57.09	62.04
CB-PSK	14.65	39.48	78.92	60.52
nBA-PSK	2.60	24.22	49.42	75.78
IPA-PSK	2.40	20.34	49.19	79.66

and IPA-PSK films are 57.09, 78.92, 49.42, and 49.19 ns, respectively, while the PL lifetime ( $\tau_2$ ) of TAA-PSK film increases to 80.82 ns, which indicates slower charge recombination. Previous studies have shown that there will be faster charge recombination and shorter PL lifetimes at the grain boundaries [40]. The longer PL lifetime implies the lower electronic trap density and fewer grain boundaries, thus leading to the greater device performance of TAA processed PD (denoted as TAA-PD). This conclusion can be confirmed by the SEM images in Fig. 5.

In order to further explore the effects of different antisolvents on the surface morphologies of the perovskite films and discover why the TAA-PD had the best performance, we analyzed the morphologies of MAPbI<sub>3</sub> films processed by different antisolvents through top-view SEM and AFM measurement (Fig. 5). The crystal grains of TL-PSK, CB-PSK, nBA-PSK, and IPA-PSK films [Figs. 5(b)–5(e)] are obviously smaller than that of the TAA-PSK film [Fig. 5(a)]. Moreover, these four kinds of antisolvent-processed perovskite films are relatively rough, forming some floccules (marked by yellow circles), which might be disordered crystallized perovskite small grains formed in the annealing process because of the polarity difference of different antisolvents. This situation is also



**Fig. 5.** Morphologies of different antisolvents processed perovskite films. (a)–(e) Top-view SEM images; the scale bar is 1  $\mu$ m. (f)–(j) AFM images; the scanned area is 5  $\mu$ m × 5  $\mu$ m, and the scale bar is 1  $\mu$ m. (k)–(o) Top-view SEM images; the scale bar is 5  $\mu$ m.



Fig. 6. Grain-size distribution histograms of films based on (a) TAA-PSK, (b) TL-PSK, (c) CB-PSK, (d) nBA-PSK, and (e) IPA-PSK measured by SEM images with the scale bar of 1  $\mu$ m.

obvious in the SEM images with the scale bar of 5  $\mu$ m [Figs. 5(k)-5(o)], while the TAA-PSK film has better crystallinity, resulting in larger grain sizes and a smoother and pinperovskite surface. The reason hole-free for this phenomenon might be that the pure MAI  $\cdot$  PbI<sub>2</sub>  $\cdot$  DMSO intermediate phases were interrupted because of the lower or higher polarity of TL, CB, nBA, and IPA, resulting in the inhomogeneous nucleation and uncontrollable disordered crystallization of perovskite in the thermal annealing process, while the moderate polarity of TAA is more conductive to the formation of a pure intermediate phase, thus leading to the formation of high-quality perovskite films. The grain-size distribution histograms of perovskite films based on these antisolvents measured by SEM with the scale bar of 1  $\mu$ m are plotted in Fig. 6. Furthermore, the AFM images of TAA-PSK, TL-PSK, CB-PSK, nBA-PSK, and IPA-PSK films are plotted in Figs. 5(f)-5(j), and the corresponding root mean square surface roughnesses are 14.5, 17.5, 16.7, 20.9, and 18.4 nm, respectively. The TAA-PSK film exhibits the smallest surface roughness and indicates lesser electronic trap states and recombination, thus more effective charge transport.

The optoelectronic properties of the perovskite PDs processed by different antisolvents were measured in dark condition and under the illumination of a 532 nm laser. Figure 7(a) shows the current variation of PDs processed by different antisolvents with the change of applied bias voltage under the illumination of  $6.37 \text{ mW/cm}^2$ . The figure shows that the dark current of TAA-PD is smaller than that of PDs processed by the other antisolvents and even one order of magnitude lower than that of IPA processed PD (denoted as IPA-PD) with the worst dark current performance. Remarkably, the photocurrent of TAA-PD is also one order of magnitude higher than that of the PDs in comparison groups under the illumination, which indicates that TAA is indeed a good antisolvent that can significantly enhance the performance of perovskite PDs. The reason for this improvement is considered to be that TAA-PSK film has better crystalline and morphological characteristics compared with the other antisolvent-processed films, which effectively inhibits the recombination losses caused by grain boundaries and defects, thus resulting in lower dark current and higher photocurrent. In order to further study the dependence of photocurrent on illumination intensity of



**Fig. 7.** Electrical properties of PDs. (a) *I-V* characteristics of the PDs processed by different antisolvents in dark condition and the illumination of 532 nm laser with a power density of 6.37 mW/cm<sup>2</sup>. (b) *I-V* characteristics of the TAA-PD under the illumination of 532 nm laser with different power densities. (c) Dependences of photoresponsivity of the PDs processed by different antisolvents on the incident power density at 532 nm;  $V_{\text{Bias}} = -2$  V. (d) Dependences of detectivity of the PDs processed by different antisolvents on the incident power density at 532 nm;  $V_{\text{Bias}} = -2$  V. (e) Dependences of EQE of the PDs processed by different antisolvents on the incident power density at 532 nm;  $V_{\text{Bias}} = -2$  V. (f) Dependences of photocurrent of the PDs processed by different antisolvents on the incident power density at 532 nm;  $V_{\text{Bias}} = -2$  V. (f) Dependences of photocurrent of the PDs processed by different antisolvents on the incident power density at 532 nm;  $V_{\text{Bias}} = -2$  V. (f) Dependences of photocurrent of the PDs processed by different antisolvents on the incident power density at 532 nm;  $V_{\text{Bias}} = -2$  V. (f) Dependences of photocurrent of the PDs processed by different antisolvents on the incident power density at 532 nm;  $V_{\text{Bias}} = 0$  V. The linear goodness values of the fitted curves are in brackets.

TAA-PD, the *I-V* curves illuminated by the 532 nm laser with different power densities are depicted in Fig. 7(b). It can be observed that the photocurrent increased significantly with the increase of power density, especially because four orders of magnitude increasement occurs compared with the dark state when the power density is 6366.20  $\mu$ W/cm<sup>2</sup>, indicating that the TAA-PD has a good photocurrent response. As a control, the I-V characteristics of TL processed PD (denoted as TL-PD), CB processed PD (denoted as CB-PD), nBA processed PD (denoted as nBA-PD), and IPA-PD under the illumination of 532 nm laser with different power densities are plotted in Figs. 9(a)-12(a), respectively. As can be seen from the figures, with the increase of incident power densities, the photocurrent of the comparison groups of PDs all shows obviously powerdependent characteristics. Interestingly, when the power density is 6366.20  $\mu$ W/cm<sup>2</sup>, the photocurrent of CB-PD with the best performance in comparison groups is about two orders of magnitude higher than the corresponding dark current but is still about four orders of magnitude lower than the

Table 2. Performance	Parameters	of PPDs with	Vertical Stru	cture
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Device Structure	Wavelength (nm)	Responsivity (A/W)	Detectivity (Jones)	Response Time Rise/Fall Time	References
TO DEDOT DSS /CH NH DH /DCD/A1	500	0.97	0.11011	/26.1.00	[42]
$110/red01.rss/Ch_3Nh_3rbl_3/rCdN/bCr/Al$	500	0.0/	9.1 × 10	$-120.1 \ \mu s$	[42]
ITO/TiO <sub>2</sub> /PCBM/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /P <sub>3</sub> HT/MoO <sub>3</sub> /Ag	500	0.34	$4.8 \times 10^{12}$	-	[43]
FTO/TiO <sub>2</sub> /AlO <sub>3</sub> /PCBM/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /Spiro/Au/Ag	600	0.4	$\sim 10^{12}$	1.2 μs/3.2 μs	[44]
ITO/PEDOT:PSS/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /PCBM/Al	670	0.314	_	4 μs/3 μs	[45]
ITO/PEDOT:PSS/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /PCBM/AZO/Al	700	0.3	_	_	[46]
FTO/TiO <sub>2</sub> /CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /Spiro/Au	660	0.18	$6.3 \times 10^{10}$	_	[47]
ITO/PEDOT:PSS/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /PCBM/BCP/Ag(TAA-PSK)	532	1.56	$1.47 \times 10^{12}$	204 ns/358 ns	This work
ITO/PEDOT:PSS/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /PCBM/BCP/Ag(TL-PSK)	532	0.46	$1.78 \times 10^{11}$	320 ns/720 ns	This work
ITO/PEDOT:PSS/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /PCBM/BCP/Ag (CB-PSK)	532	0.61	$2.58 \times 10^{11}$	304 ns/656 ns	This work
ITO/PEDOT:PSS/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /PCBM/BCP/Ag (nBA-PSK)	532	0.35	$1.56 \times 10^{11}$	348 ns/768 ns	This work
ITO/PEDOT:PSS/CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> /PCBM/BCP/Ag (IPA-PSK)	532	0.30	$1.48\times10^{11}$	364 ns/744 ns	This work

photocurrent of TAA-PD, indicating TAA is superior to the other four antisolvents in improving the device performance.

Responsivity (R) as a crucial figure of merit to evaluate the performance of the PDs can be calculated by the equation [41]

$$R = \frac{I_{\rm ill} - I_{\rm dark}}{AE_{\rm e}},\tag{2}$$

where  $I_{\rm ill}$  and  $I_{\rm dark}$  represent the photocurrent and dark current, respectively, A is the effective illumination area  $(0.04 \text{ cm}^2)$ , and  $E_e$  is the power density of the incident light. Figure 7(c) plots R as a function of  $E_e$  using a doublelogarithmic scale at the applied bias of -2 V. A linear dependence between  $\log(R)$  and  $\log(E_{e})$  is observed for all of the PDs, and the values of R decrease with the increase of power density. Under a weak illumination of 6.37  $\mu$ W/cm<sup>2</sup>, the TAA-PD shows the best performance with an R value of 1.56 A/W, which is a good responsivity for PDs with the same vertical structures and only MAPbI<sub>3</sub> perovskite as the photosensitive layer. The other four control groups obtain R values of 0.46 A/W (TL-PD), 0.61 A/W (CB-PD), 0.35 A/W (nBA-PD), and 0.30 A/W (IPA-PD), respectively. The key performance parameters of this work and previously reported PDs with similar vertical structures and using MAPbI<sub>3</sub> perovskite as the single photosensitive material are summarized in Table 2, which indicates that the TAA-PD exhibits better device performance than the reported works and the other four antisolvent-processed PDs in comparison groups of this work. In addition to the responsivity, the specific detectivity  $(D^*)$  is another critical performance parameter to characterize the sensitivity of a PD and can be expressed as [48]

$$D^* = R \cdot \sqrt{\frac{A}{2eI_{\text{dark}}}},\tag{3}$$

where  $I_{dark}$  is the dark current. As plotted in Fig. 7(d), the values of  $D^*$  show linear dependence on the power density of incident light similar to the *R* curves. It is worth noting that the TAA-PD has a significant performance advantage over the other comparison groups in terms of the  $D^*$  values. Under the illumination of 6.37  $\mu$ W/cm<sup>2</sup>, the  $D^*$  of TAA-PD reaches  $1.47 \times 10^{12}$  Jones, which is much higher than that of PDs processed by TL, CB, nBA, and IPA, corresponding to the  $D^*$  values of  $1.78 \times 10^{11}$  Jones,  $2.58 \times 10^{11}$  Jones,  $1.56 \times 10^{11}$  Jones, and  $1.48 \times 10^{11}$  Jones, respectively. As one of the important

indexes of PDs, external quantum efficiency (EQE) is often used to evaluate the efficiency of PDs to generate free carriers by absorbing photon energy and can be calculated by [49]

$$EQE = R \times \frac{hc}{e\lambda} \times 100\%,$$
 (4)

where *h* is the Planck's constant, *c* is the velocity of light, and  $\lambda$  represents the wavelength of incident light. In Fig. 7(e), the maximum EQE value 363.56% is obtained by TAA-PD when the power density is 6.37  $\mu$ W/cm<sup>2</sup> and the bias is –2 V. With the increase of power density, the EQE shows a linear decreasing dependence. The EQE values of PDs processed by TL, CB, nBA, and IPA are 107.98%, 140.95%, 82.63%, and 71.18% under the same conditions. The LDR is a crucial figure of merit for PDs to evaluate the detection range in which the current response is linear with the light intensity. It can be given in a logarithmic scale as [13]

$$LDR = 20 \log \frac{I_{upper} - I_{dark}}{I_{lower} - I_{dark}},$$
(5)

where  $I_{\rm upper}$  and  $I_{\rm lower}$  represent the upper and lower photocurrent values at which the current response deviates from linearity, respectively. Figure 7(f) plots the LDR curves measured under the illumination of a 532 nm laser, and, with the range of light intensities from 254.78 nW/cm<sup>2</sup> to 178.34 mW/cm<sup>2</sup>, the bias is 0 V. The corresponding LDR of TAA-PD is 110 dB, which is higher than the corresponding values of 105 dB (TL-PD), 106 dB (CB-PD), 100 dB (nBA-PD), and 91 dB (IPA-PD) in comparison groups. All of the LDR performance of these PDs is much better than that of InGaAs PDs [42].

The photoresponse time is one of the important parameters for PDs to characterize whether the response sensitivity can follow the switching of optical signals. Figure 8(a) depicts the instantaneous photocurrent responses of the TAA-PD measured by a 532 nm laser with a cyclical ON/OFF light modulating switching at an illumination of 1.27 mW/cm<sup>2</sup>, when the bias was 0 V. The device exhibits high stability and long cycle repeatability, which indicates that TAA-PD has great optically controlled switching performance. The corresponding instantaneous photocurrent responses of the other four comparison groups are plotted in Figs. 9(b)–12(b). To further investigate the photoresponse time of the device, we increased the



**Fig. 8.** Photoswitching properties of the PDs. (a) Photoswitching characteristics of the TAA-PD measured alternately in dark and under 532 nm laser illumination (1.27 mW/cm<sup>2</sup>,  $V_{\text{Bias}} = 0$  V). (b) The switching time of the TAA-PD during one ON/OFF illumination switching cycle. (c) Photocurrent stability measurement of TAA-PD for 1000 continuous switching cycles. Photoswitching characteristics of the TAA-PD under (d) 532 nm, (e) 405 nm, and (f) 808 nm laser illumination with different power densities. (g) Photoswitching characteristics of the PDs processed by different antisolvents measured alternately in dark and under 532 nm laser illumination (1.27 mW/cm<sup>2</sup>,  $V_{\text{Bias}} = 0$  V). (h) Photoswitching characteristics of the PDs processed by different antisolvents measured alternately in dark and under 532 nm laser illumination (1.27 mW/cm<sup>2</sup>,  $V_{\text{Bias}} = 0$  V). (k) Photoswitching characteristics of the PDs processed by different antisolvents measured alternately in dark and under 532 nm laser illumination (1.27 mW/cm<sup>2</sup>,  $V_{\text{Bias}} = 0$  V), respectively. (i) Photocurrent distribution of the PDs processed by different antisolvents measured alternately in dark and under 405, 532, and 808 nm laser illumination (1.27 mW/cm<sup>2</sup>,  $V_{\text{Bias}} = 0$  V), respectively. (j) Test schematic diagram of response time.

modulation frequency of pulsed laser signal to 100 kHz. As shown in Fig. 8(b), the rise time ( $t_{rise}$ , defined as the time interval between 10% and 90% of the maximum photocurrent) and fall time ( $t_{fall}$ , defined as the time interval between 90% and 10% of the maximum photocurrent) measured by oscillo-scope are 204 and 358 ns, respectively, which are comparable or superior to those previously reported perovskite bulk heterojunction PDs [49] and are of great significance for optical communication, photoelectric imaging, and other applications. The response times of corresponding comparison groups are TL-PD ( $t_{rise} = 320$  ns,  $t_{fall} = 720$  ns), CB-PD ( $t_{rise} = 304$  ns,

 $t_{\text{fall}} = 656 \text{ n}$ ), nBA-PD ( $t_{\text{rise}} = 348 \text{ ns}$ ,  $t_{\text{fall}} = 768 \text{ ns}$ ), and IPA-PD ( $t_{\text{rise}} = 364 \text{ ns}$ ,  $t_{\text{fall}} = 744 \text{ ns}$ ), respectively, and are plotted in Figs. 9(c)-12(c). The  $f_{-3 \text{ dB}}$  of a PD and its corresponding  $t_{\text{rise}}$  are related as follows [50]:

$$f_{-3\,\mathrm{dB}} = \frac{0.35}{t_{\mathrm{rise}}},$$
 (6)

where the  $f_{-3 \text{ dB}}$  of TAA-PD is 1.72 MHz, and the  $f_{-3 \text{ dB}}$  of corresponding comparison groups are 1.09 MHz (TL-PD), 1.15 MHz (CB-PD), 1.01 MHz (nBA-PD), and 0.96 MHz (IPA-PD), respectively. In addition, the high stability of



**Fig. 9.** Electrical and photoswitching properties of TL-PD. (a) *I-V* characteristics under the illumination of 532 nm laser with different power densities. (b) Photoswitching characteristics measured alternately in dark and under 532 nm laser illumination (1.27 mW/cm<sup>2</sup>,  $V_{\text{Bias}} = 0$  V). (c) Switching time of the TL-PD during one ON/OFF illumination switching cycle. Photoswitching characteristics under (d) 532 nm, (e) 405 nm, and (f) 808 nm laser illumination with different power densities.

ON/OFF switching is of great importance for the practical application of PDs. Therefore, we tested the photocurrent response of TAA-PD for 1000 switching cycles under the illumination of 1.27 mW/cm<sup>2</sup> at the bias of 0 V [Fig. 8(c)] and found there is no significant change during the measurement, thus indicating excellent stability and repeatability of the TAA-PD. Figure 8(d) shows the photoswitching characteristics of TAA-PD under 532 nm laser illumination and with different incident power densities. The photocurrent increases linearly with the increasement of power densities, which is consistent with the results in Fig. 7(f), and the TAA-PD can realize effective optical switch response under different power densities ranging from 254.78 nW/cm<sup>2</sup> to 178.34 mW/cm<sup>2</sup>. Figures 8(e) and 8(f) show the photoswitching characteristics of TAA-PD illuminated by different power densities at 405 and 808 nm, respectively. Further, the photoswitching characteristics of the other four comparison groups under the illumination of 532, 405, and 808 nm with different power densities are plotted in Figs. 9(d)-12(d), 9(e)-12(e), and 9(f)-12(f).

Meanwhile, as a control, we studied the photoswitching characteristics of the five PDs under the 532 nm laser illumination of  $1.27 \text{ mW/cm}^2$  at the bias of 0 V; the results are shown in Fig. 8(g). Compared with the other four comparison groups, TAA-PD has a more prominent photocurrent response under the same light conditions, indicating that TAA as an



**Fig. 10.** Electrical and photoswitching properties of CB-PD. (a) *I-V* characteristics under the illumination of 532 nm laser with different power densities. (b) Photoswitching characteristics measured alternately in dark and under 532 nm laser illumination  $(1.27 \text{ mW/cm}^2, V_{\text{Bias}} = 0 \text{ V})$ . (c) Switching time of the CB-PD during one ON/OFF illumination switching cycle. Photoswitching characteristics under (d) 532 nm, (e) 405 nm, and (f) 808 nm laser illumination with different power densities.

antisolvent to modify perovskite has great advantages compared with other antisolvents, which can effectively improve the quality of perovskite film and thus improve the photoelectric performance of the PD. In order to further understand the photoswitching characteristics of PDs, we also measured the photoresponse of the PDs under 405 and 808 nm laser illumination with a specific incident power density of  $1.27 \text{ mW/cm}^2$ and bias voltage of 0 V and compared the result with the photoresponse illuminated by 532 nm. As shown in Fig. 8(h), all PDs processed by different antisolvents have noticeable and fast photocurrent response under the illumination of three wavelengths of lasers. Remarkably, the photoswitching performance of TAA-PD under three wavelengths of illumination is significantly better than that of other comparison groups, further proving that the TAA is superior to TL, CB, nBA, and IPA in improving the performance of perovskite PDs; further, the histograms corresponding to the photocurrent response under three wavelengths of light irradiation given in Fig. 8(i) confirm this conclusion more intuitively. In addition, all PDs are more sensitive to the 532 nm laser, and the photocurrent response intensity to 405 and 808 nm light illumination decreases in turn, which is consistent with the absorption spectra in Fig. 4(a). Figure 8(j) displays the schematic diagram of the response time test system of the PDs. The pulse frequency of laser was controlled by a signal generator and was 100 kHz in



**Fig. 11.** Electrical and photoswitching properties of nBA-PD. (a) *I-V* characteristics under the illumination of 532 nm laser with different power densities. (b) Photoswitching characteristics measured alternately in dark and under 532 nm laser illumination  $(1.27 \text{ mW/cm}^2, V_{\text{Bias}} = 0 \text{ V})$ . (c) Switching time of the nBA-PD during one ON/OFF illumination switching cycle. Photoswitching characteristics under (d) 532 nm, (e) 405 nm, and (f) 808 nm laser illumination with different power densities.

this work. The pulse laser converged through lenses  $M_1$  and  $M_2$ and then illuminated to the perovskite PDs that connected to an oscilloscope with 50  $\Omega$  input resistance compensation after being restrained by an aperture diaphragm of proper size. The analog signals of response time were obtained by the oscilloscope monitoring.

# 4. CONCLUSIONS

In summary, we developed an effective solution-processed method for the fabrication of high-performance organometal trihalide PPDs. By introducing the novel and environmentfriendly TAA as antisolvents for the first time, the responsivity of the PD reached 1.56 A/W under 532 nm laser illumination of 6.37  $\mu$ W/cm<sup>2</sup>, which is good responsivity for PPDs with the vertical structure of glass/ITO/PEDOT:PSS/MAPbI<sub>3</sub>/ PC<sub>61</sub>BM/BCP/Ag. The superior performance of the TAA-PD compared with other PDs in the comparison groups is mainly ascribed to the better modification-assisted selectivity characteristics of TAA with moderate polarity than those of the other antisolvents, which would effectively regulate the formation of an intermediate phase staged in between a liquid precursor phase and a solid perovskite phase and further promote the homogeneous nucleation and crystal growth in the subsequent



**Fig. 12.** Electrical and photoswitching properties of IPA-PD. (a) *I-V* characteristics under the illumination of 532 nm laser with different power densities. (b) Photoswitching characteristics measured alternately in dark and under 532 nm laser illumination  $(1.27 \text{ mW/cm}^2, V_{\text{Bias}} = 0 \text{ V})$ . (c) Switching time of the IPA-PD during one ON/OFF illumination switching cycle. Photoswitching characteristics under (d) 532 nm, (e) 405 nm, and (f) 808 nm laser illumination with different power densities.

annealing process, thus leading to the formation of high-quality perovskite films and enhanced PD performance. Moreover, compared with traditional antisolvents such as TL, CB, nBA, and IPA, TAA has less toxicity, which is more beneficial for management of the environment and health in the preparation process. Together, with the characteristics of low cost and easy availability, TAA is a great environment-friendly antisolvent with remarkable advantages for the fabrication of highperformance PPDs in the future and could provide a reference for similar research work.

**Funding.** National Natural Science Foundation of China (61675147, 61735010, 91838301); National Key Research and Development Program of China (2017YFA0700202); Department of Education of Guangdong Province (2018KQNCX264); Basic Research Program of Shenzhen (JCYJ20170412154447469); Beiyang Yong Junior Faculties of Tianjin University (2019XRG-0056); Wenzhou City Governmental Public Industrial Technology Project (G20160014).

**Disclosures.** The authors declare no conflicts of interest.

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