Supporting Information

Sensitive Self-powered perovskite photodetector by noise suppression with poly(vinylidene fluoride-trifluoroethylene) doping for defects passivation

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Supplementary Note 1

\textit{DFT calculations}: The first principles computations were carried out by Vienna Ab initio Simulation Package (VASP) based on density functional theory. Generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was used to describe the exchange-correlation interaction. The projector augmented wave pseudopotentials were adopted to describe the ion-electron with a cutoff energy of 500 eV. The K-point grid of Brillouin zone was tested and sampled by 3×3×1 within Gamma-Pack. The electronic energy and forces were converged to within 10^{-5} eV and 0.03 eVÅ\textsuperscript{-1}, respectively. The electrostatic potentials (\(\phi\)) of the molecule were calculated using the Gaussian 09 package at the B3LYP/def2TZVP level with DFT-D3.

Supplementary Note 2

The capacitance–voltage (C-V) curves were monitored by varying the voltage from 0.1 to 1.5 V at a frequency of 2 kHz. The capacitance-frequency (C-f) measurements were performed with a sweeping frequency from 1 MHz to 100 Hz (20 mV AC voltage). The two measurements were done in the dark under air conditions. The energetic profile of trap density of states (tDOS) can be derived from C-f curves using the equation:

\[ N_T(E_\omega) = \frac{V_{bi} dC}{q W_0 k_B T} \frac{\omega}{\omega_0} \]

(1)

\[ E_\omega = k_B T \ln \left( \frac{\omega_0}{\omega} \right) \]

(2)
where $V_{bi}$ is the built-in potential, $W$ is the depletion width, $q$ is the elementary charge, $C$ is the capacitance, $\omega$ is the applied angular frequency, $k_B$ is the Boltzmann’s constant, $T$ is the temperature, and $\omega_0$ is the attempt-to-escape frequency.\(^2\)

The tDos profiling ($N_t(x)$) can be calculated as a function of profiling distance $x = \varepsilon_0 \varepsilon_r A/C$ from the Schottky junction using the CV results by:

$$N_t(x) = -\frac{2}{q \varepsilon_0 \varepsilon_r A^2} \left( \frac{dC(x)}{dV} \right)^{-1}$$

$\varepsilon_r$ is the dielectric constant of the sample, $\varepsilon_0$ is the dielectric constant in a vacuum, and $A$ (0.04 cm$^2$) is the active area.

Supplementary Note 3

**Materials and Reagents:** The etching indium tin oxide (ITO) glass sheets (RS $\approx 8$ $\Omega$/sq) were purchased from Advanced Election Technology CO., Methylammonium Iodide (MAI, 99.5%), Formamidinium iodide (FAI, 99.9%), Lead Iodide (PbI$_2$, 99.9%), methylammonium chloride (MACl, 99.9%), cesium chloride (CsCl, 99.9%), 2, 2$''$, 7, 7$''$-Tetrakis [N, N-di(4-methoxyphenyl) amino]-9, 9$''$-Spirobifluorene (Spiro-OMeTAD, 99.9%), bis (trifluoromethyl sulfonyl)-imide lithium salt (Li-TFSI) and 4-test-butyl pyridine (4-TBP, 96%) were purchased from Xi’an Yuri Solar Co., Ltd. SnO$_2$ (Tin (IV) oxide, 15% in H2O) colloidal dispersion liquid was purchased from Alfa Aesar. Dimethylsulfoxide (DMSO, 99.9%), N, N-dimethylformamide (DMF, 99.9%), chlorobenzene (CB, 99.9%). were purchased from Sigma–Aldrich.

The SnO$_2$-KCl solution was prepared by mixing 15% SnO$_2$ hydrocolloid solution with 10 mg mL$^{-1}$ KCl solution at a volume ratio of 1:1. The mixed solution was stirred for 2 h, then filtered by a 0.22 $\mu$m syringe filter before use. A precursor solution of FA$_{0.9}$MA$_{0.05}$Cs$_{0.05}$PbI$_3$ was prepared by weighing PbI$_2$ 557.82 mg, FAI 179.7 mg, MAI 8.73 mg, CsCl 9.225 mg and 14.85 mg MACl then dissolving them in a 1mL mixed solvent of DMSO and DMF (volume ratio 1:4). The precursor solution was stirred for at least 12 h, then filtered by a 0.22 $\mu$m syringe filter before use. Dissolve 72.3 mg Spiro-OMeTAD in 1 mL chlorobenzene, stirred for 20 min, then add 17.5 $\mu$L Li-TFSI
(520 mg Li-TFSI dissolved in 1 mL acetonitrile) and 28.5 μL TBP, the Spiro-OMeTAD solution could be obtained by stirring at room temperature for 12 h. P(VDF-TrFE) was dissolved in a mixture of DMF and DMSO (DMF:DMSO=4:1) at concentrations of 0.05 mg mL\(^{-1}\), 0.1 mg mL\(^{-1}\) and 0.15 mg mL\(^{-1}\). PVT is completely dissolved and added to the precursor solution.

**Device Fabrication:** The ITO was cleaned by ultrasonication in a cleaning liquid, deionized water, acetone, and anhydrous ethanol for 30 min, respectively, and then dried with nitrogen flow before use. The ITO glass substrates were treated with UV ozone for 30 min before depositing the SnO\(_2\) layer. The prepared SnO\(_2\)-KCL solution was spin-coated onto the ITO substrate at 4000 rpm for 20 s followed by annealing at 150 °C for 20 min. For modified ITO glass/SnO\(_2\), then the ITO glass/SnO\(_2\) substrates were transferred into glove box. The prepared perovskite precursor solution was spin-coated on the modified ITO glass/SnO\(_2\) substrate at 4000rpm for 30s where 200μL of CB anti-solvent was dripped on the perovskite films at 10 s before ending the program. The samples were then annealed at 120 °C for 30 min. we spin-coated the prepared PEAI onto the perovskite film surface (3000 rpm, 20 s). To fabricate the hole transport layer (HTL), we spin-coated the prepared Spiro-OMeTAD precursor onto the PEAI film surface (5000 rpm, 20 s). Subsequently, we deposited a silver electrode, approximately 100 nm in thickness, onto the HTL using vacuum thermal evaporation.

**Characterization and Measurements:** TEM measurement was carried out by Talos F200X. XRD intensities were measured using XRD (Shimadzu XRD-6100 diffractometer with Cu K\(_{α}\) radiation). Absorbance spectra of the perovskite films were measured by a UV-visible spectrophotometer (UV 2600, shimadzu, Japan).

A semiconductor parameter analyzer (Platform Design Automation, Inc. FS380 ProTM) coupled with a four-probe station (MINI, Shenzhen Zhanxin) in ambient air were used to measure electrical characterization including time dependent J-V feature, Cp-V, Cp-f. Fiber laser diode (wavelength of 685 nm) driven by a controller (DC4104, Thorlab) were used as light source. All the signals were controlled by a function/arbitrary waveform generator (Keysight 3210A). Photo-response time testing was acquired by an oscilloscope (Tektronix, MS054 5-BW-1000). The active area of
photodetector was determined to be 0.04 cm$^{-2}$ by a mental mask. The spectral responsivity measurement was carried out on an EQE system (Newport, USA).

Supplementary Note 4

Crystallinity calculation:

$$X_c = \frac{I_c}{I_{a100}} \times 100\%$$

$I_{a100}$ is the integral intensity of all diffraction peaks in the sweep area, $I_c$ the diffraction intensity of crystals isolated from the diffraction spectrum of measured samples.
Figure S1. Time-dependent photocurrent response curves of detector with the content of PVT 0-0.15 mg mL$^{-1}$. 
Figure S2. UV-visible absorption curves of films with the content of PVT 0-0.15 mg mL\(^{-1}\).
Figure S3. XRD curves of films with the content of PVT 0-0.15 mg mL$^{-1}$. 
Figure S4. (a) Mott-Schottky curves of the PDs with and without PVT, (b) frequency-capacitance curves of the PDs with and without PVT, (c) Trap density of states (tDOS) for devices without and with PVT.
Figure S5. the cross-sectional SEM image of the device.
Figure S6. External Quantum Efficiency (EQE) variation curves of the PDs with and without PVT.
Figure S7 (a) Narrow wavelength D* of a device with PVT passivation; (b) Schematic illustration of pulse tests; (c) measurements of the heartbeat signal pattern of a finger under 685 nm light.
Figure S8. response time of photodetector without PVT
References

