

Supporting information

Near-Infrared Polarization-Sensitive Photodetection via Interfacial Symmetry Engineering of Si/MAPbI₃ Heterostructural Single Crystal

Jianbo Wu^{a, b}, Xinyuan Zhang^{a, b}, Ziyang Wang^a, Lishan Liang^a, Xinyi Niu^a, Qianwen Guan^{a, b}, Shihai You^a, and Junhua Luo^{*a, b, c}

a J. Wu, X. Zhang, Z. Wang, L. Liang, X. Niu, Q. Guan, S. You, Prof. J. Luo
State Key Laboratory of Structural Chemistry
Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences
Fuzhou, Fujian 350002, P. R. China
E-mail: jhluo@fjirsm.ac.cn

b J. Wu, X. Zhang, Q. Guan, Prof. J. Luo
University of Chinese Academy of Sciences
Beijing 100049, P. R. China

c Prof. J. Luo
School of Chemistry and Chemical Engineering
Jiangxi Normal University
Nanchang, Jiangxi 330022, P. R. China

Experimental Section

Materials: The materials used were lead iodide (PbI_2 , Aladdin Chemistry Co., Ltd., 99.9%), methylamine iodide (MAI, self-synthesized), γ -butyrolactone (GBL, Shanghai Tichem Chemical Co., Ltd, 99.8%), (3-aminopropyl)triethoxysilane (APTES, Aladdin Chemistry Co., Ltd., >99%), 1,2-dichlorobenzene (DCB, Aladdin Chemistry Co., Ltd., >99%), hydroiodic acid (HI, Aladdin Chemistry Co., Ltd., 48% wt/wt aq), 2-propanol (IPA, Aladdin Chemistry Co., Ltd., >99.5%)

Preparation of the precursor solutions: The raw materials 2.305 g PbI_2 and 0.795 g MAI were dissolved in 5 mL GBL solvent. A bright-yellow solution was obtained.

Growth of MAPbI_3 single crystal: MAPbI_3 single crystals were grown via inverse-temperature crystallization method. The precursor solution was transferred to a vial and then heat up to 100°C in oil bath and maintained hours under this temperature for the growth of the single crystal.

Preparation of modified Si substrate: The method of modifying Si substrate was in accordance with the previous report. The precleaned Si (n-type) wafer was placed into a mixture of DCB and APTES solvent (20:1) for 12 h at 50°C and ultrasonically rinsed with IPA to obtain NH_2 -terminated molecules on the surface. The wafer was then treated with HI (aq.) to convert the amino groups into $-\text{NH}_3\text{I}$ groups.

Growth of Si-integrated MAPbI_3 single crystal: A small droplet of the $\text{MAPbI}_3/\text{GBL}$ solution was dropped onto the modified Si wafer. Then, the Si wafer with small droplet was heat to 50°C to volatilize the solvent and obtain the seed crystal. After that, the Si wafer with the seed crystal was placed into the preheat $\text{MAPbI}_3/\text{GBL}$ solution for the growth of the Si-integrated MAPbI_3 single crystal. The solution was heated to 100°C and maintained this temperature for hours.

Powder X-ray diffraction: Powder X-ray diffraction measurement was performed on a Rigaku MiniFlex 600 diffractometer at atmosphere environment. The diffraction patterns were collected in the 2θ range of 5° – 50° with a step size of $0.5^\circ/\text{min}$.

Scanning electron microscope measurement (SEM): The SEM image was collected on ZEISS Sigma 300 field-emission scanning electron microscope operated at 3kV.

Absorption spectrum measurement: Absorption spectrums of MAPbI_3 was performed on a Perkin-Elmer Lambda 900 UV–Vis–NIR spectra photometer at room temperature. In which BaSO_4 was used as the 100% reflectance reference.

Photoluminescence spectra measurements: Emission spectra of MAPbI_3 and the MAPbI_3/Si heterojunction were performed on an Edinburgh FLS1000 fluorescence spectrometer. The lifetime of MAPbI_3 and the MAPbI_3/Si heterojunction were measured on an Edinburgh FLS1000 fluorescence spectrometer using a picosecond pulsed diode laser. The dynamics of emission decay were monitored by using the FLS1000's time-correlated single-photon counting capability (1,024 channels; 500 ns window) with data collection for 10,000 counts in the maximum channel.

Optoelectronic performances measurements: The current vs voltage (I–V) and photocurrent vs time (I–t) with light on and off (measured at zero bias) were measured using a high precision electrometer (Keithley 6517B). I–V tests were collected under the 405 nm, 520 nm, 637 nm and 785 nm continuous-wave lasers (ITC4001). I–t was collected under the 785 nm continuous-wave lasers (ITC4001). The incident light intensity was measured by light power meter.

Results and Discussion

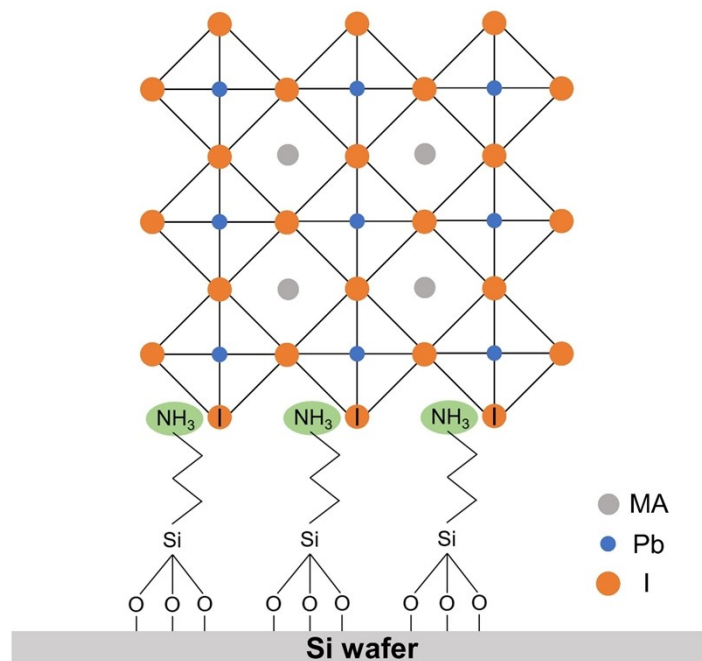


Figure S1. Schematic of the MAPbI₃/Si heterostructure

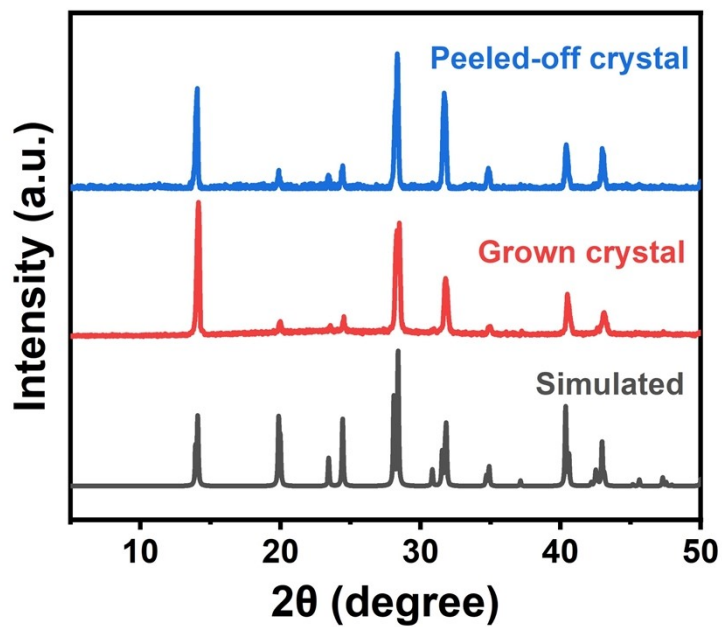


Figure S2. PXRD patterns of the simulation of MAPbI₃ crystal, naturally grown crystal, and the peeled-off MAPbI₃ crystal from the Si wafer.

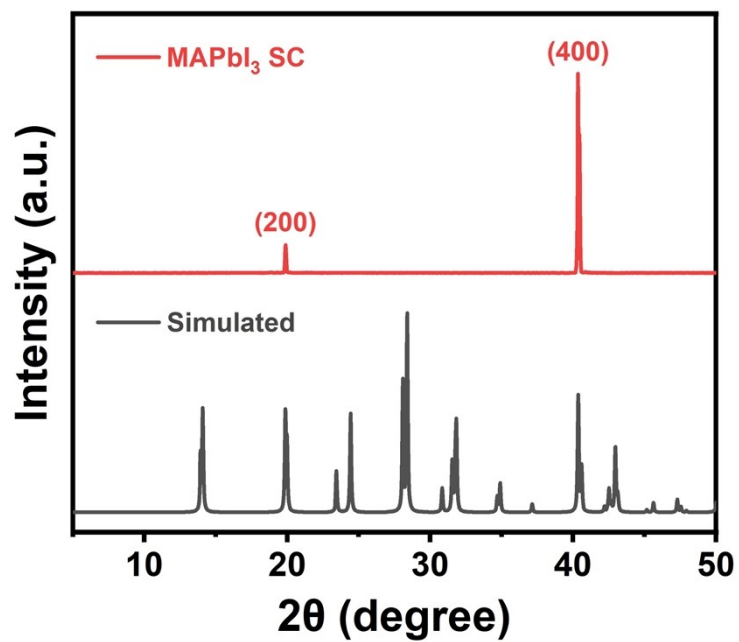


Figure S3. XRD pattern of the MAPbI₃ single crystal.

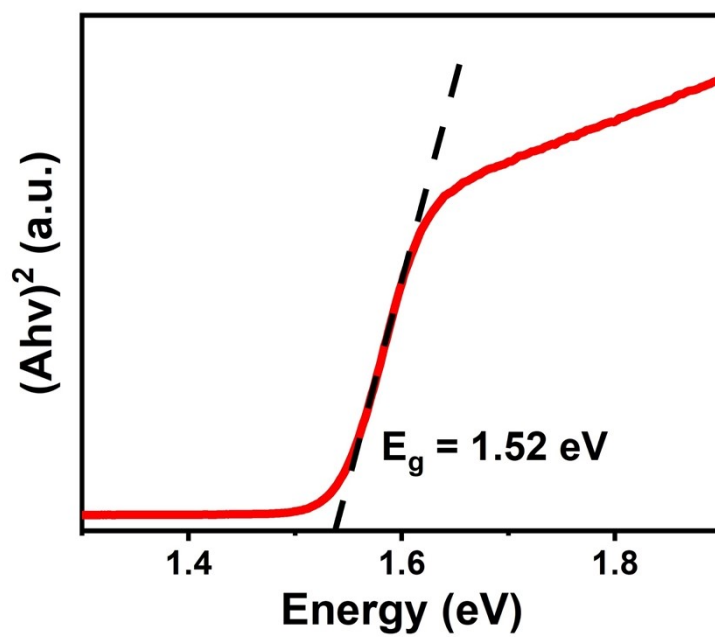


Figure S4. The calculation of MAPbI₃ optical band gap via corresponding Tauc plots.

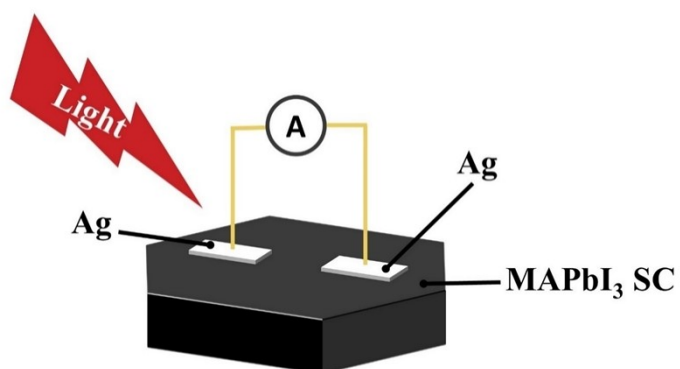


Figure S5. Schematic illustration of the MAPbI₃ SC device.

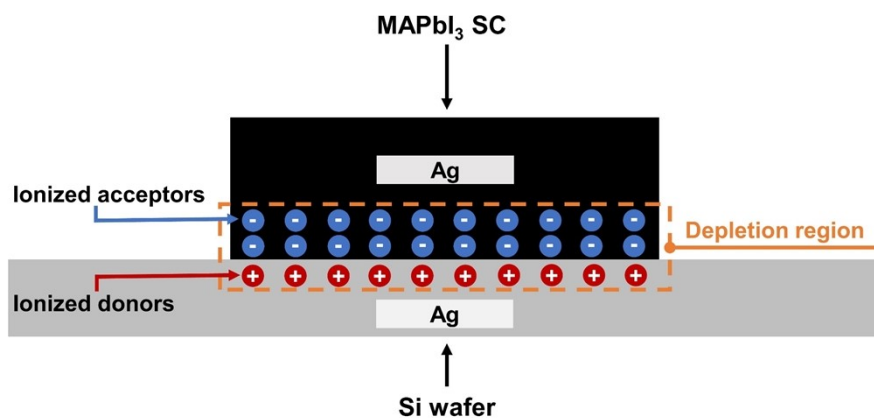


Figure S6. A schematic of depletion region at the MAPbI₃/Si heterostructure interface

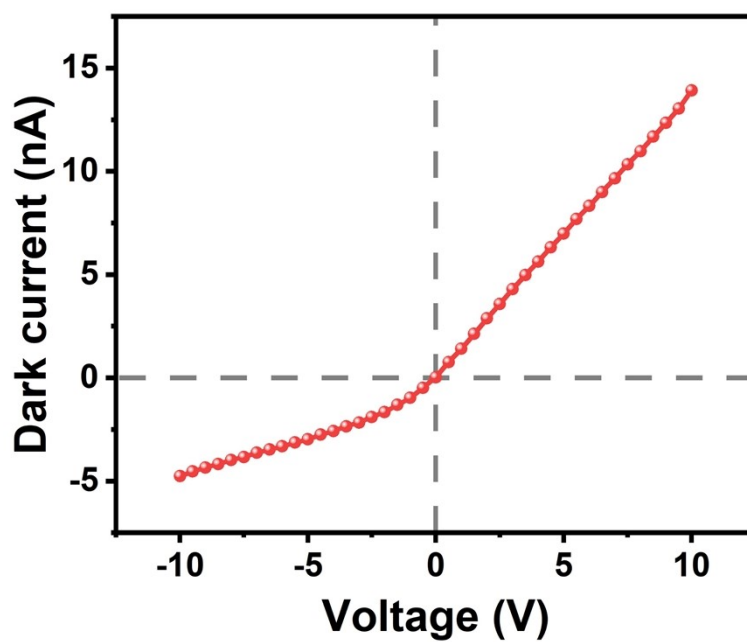


Figure S7. Dark current of the heterojunction photodetector

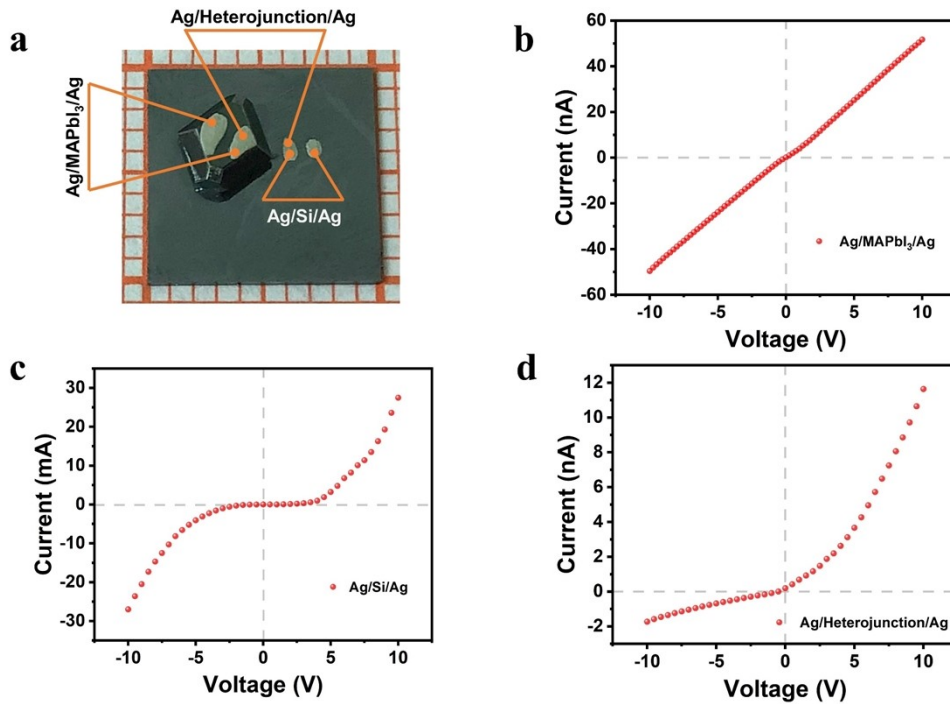


Figure S8. (a) Photograph of Ag/MAPbI₃/Ag, Ag/Si/Ag and Ag/Heterojunction/Ag device in the same heterostructure sample. (b) *I*-*V* curve of Ag/MAPbI₃/Ag under the dark condition. (c) *I*-*V* curve of Ag/Si/Ag under the dark condition. (d) *I*-*V* curve of Ag/Heterojunction/Ag under the dark condition.

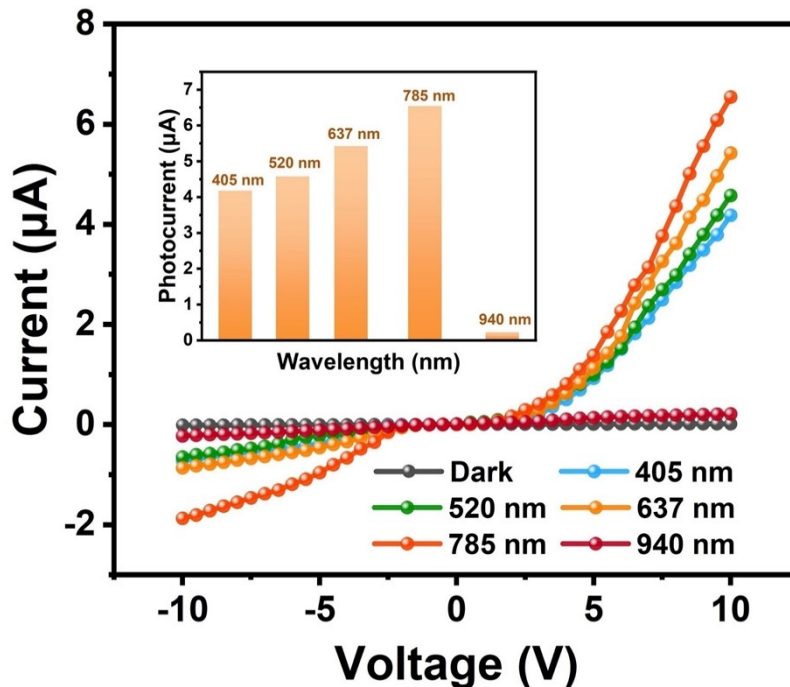


Figure S9. *I*-*V* curves of the heterojunction photodetector under the different wavelength illumination at the power density of 19.4 mW/cm². The insert shows the photocurrents of the heterojunction device as a function of wavelength.

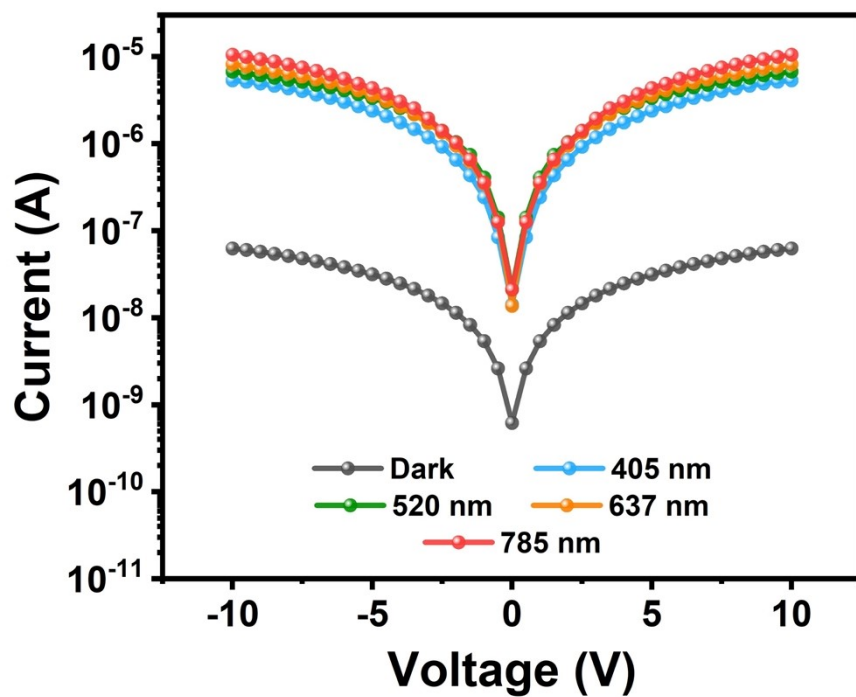


Figure S10. I - V curves of the MAPbI₃ SC photodetector under the different wavelength illumination at the power density of 19.4 mW/cm².

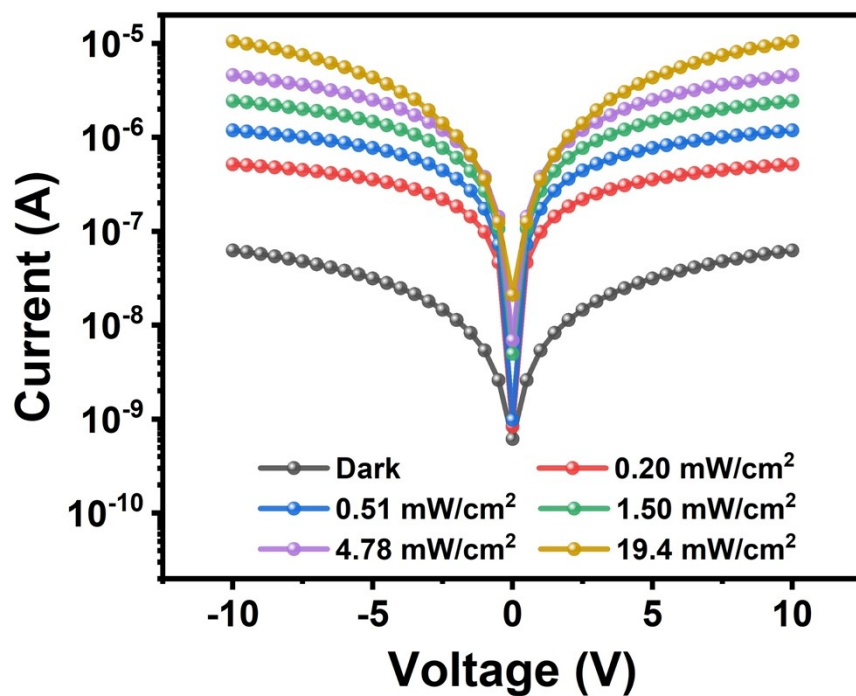


Figure S11. I - V curves of the MAPbI₃ SC photodetector under the 785 nm illumination with different power density.

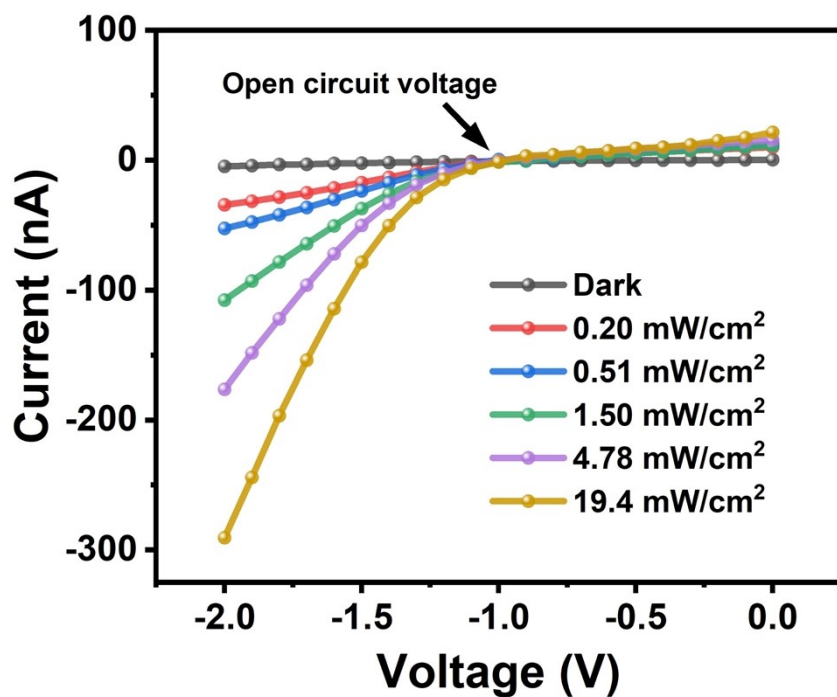


Figure S12. Open-circuit voltage of the heterojunction device.

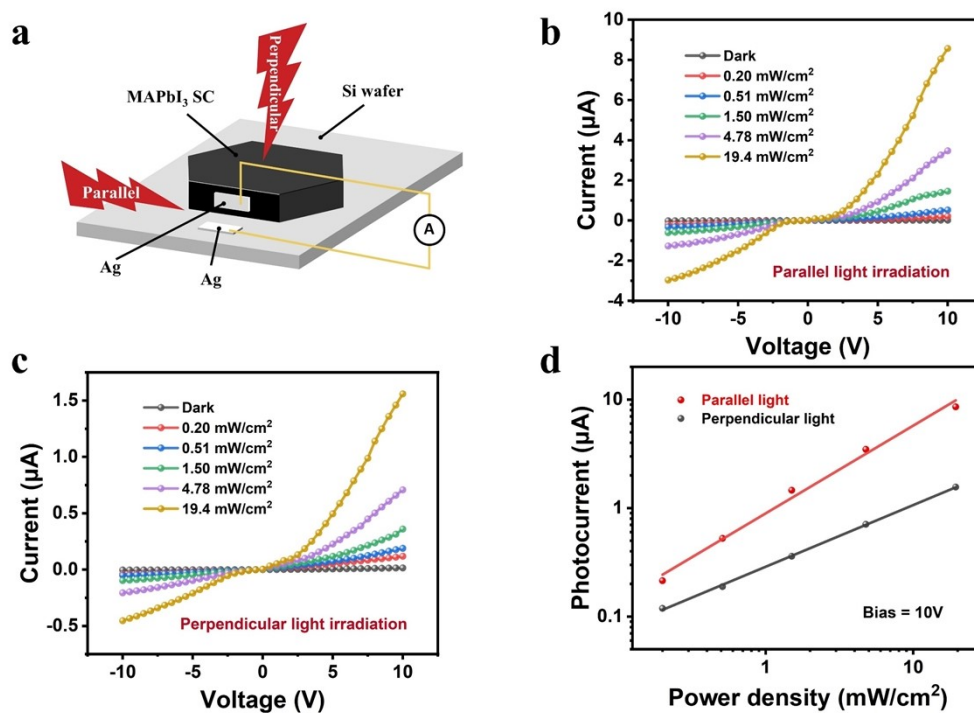


Figure S13. (a) Schematic illustration of the MAPbI₃/Si heterostructure photodetector with different incident directions. (b) *I-V* curves of heterostructure photodetector with parallel light irradiation. (c) *I-V* curves of heterostructure photodetector with perpendicular light irradiation. (d) Light power density dependent photocurrent with different incident directions.

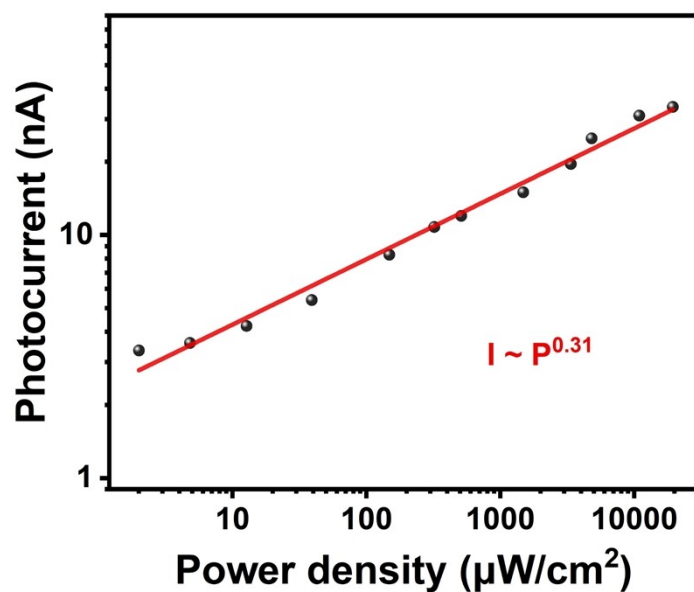


Figure S14. Light power density dependent photocurrent of the MAPbI₃/Si device under the self-driven mode.

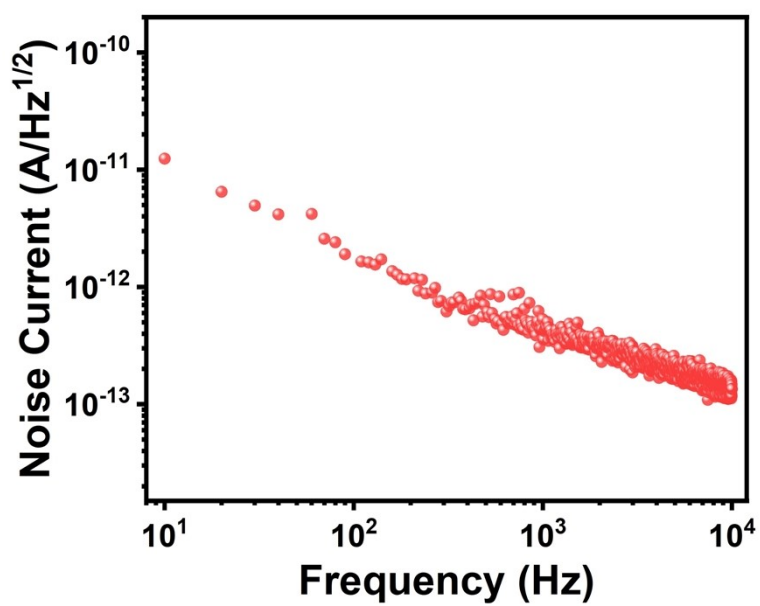


Figure S15. The current noise power spectra at 0 V bias.

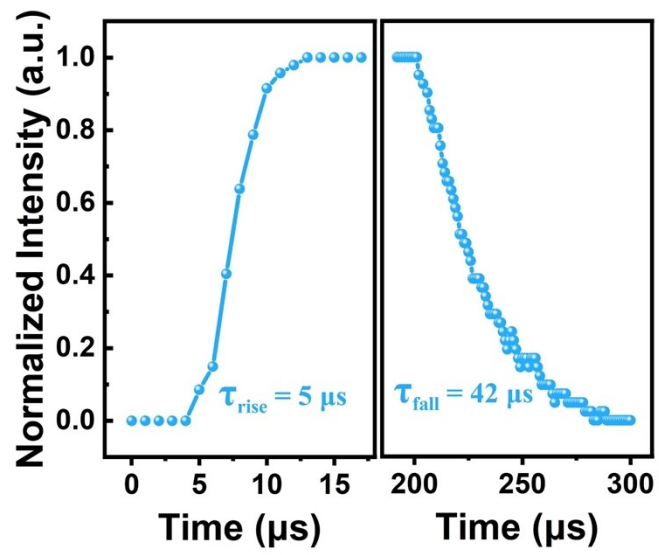


Figure S16. The response time of the heterojunction photodetector under the self-powered mode at 785 nm.

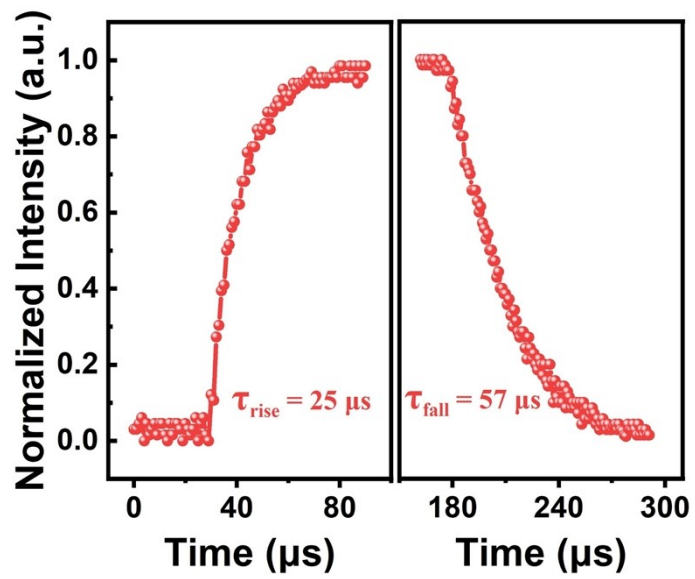


Figure S17. The response time of the heterojunction photodetector under the self-powered mode at 940 nm.

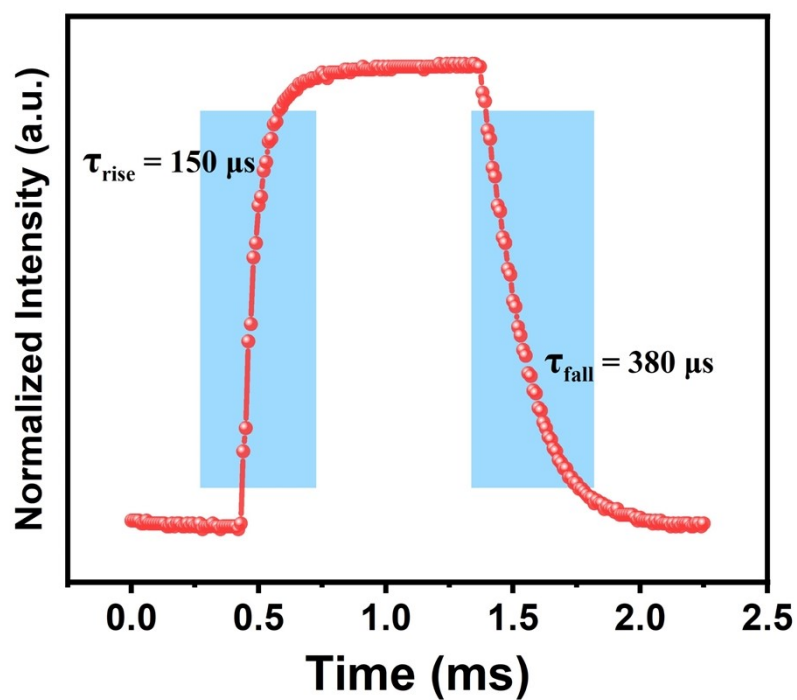


Figure S18. The response time of the MAPbI₃ SC photodetector under 10 V bias at 785 nm.

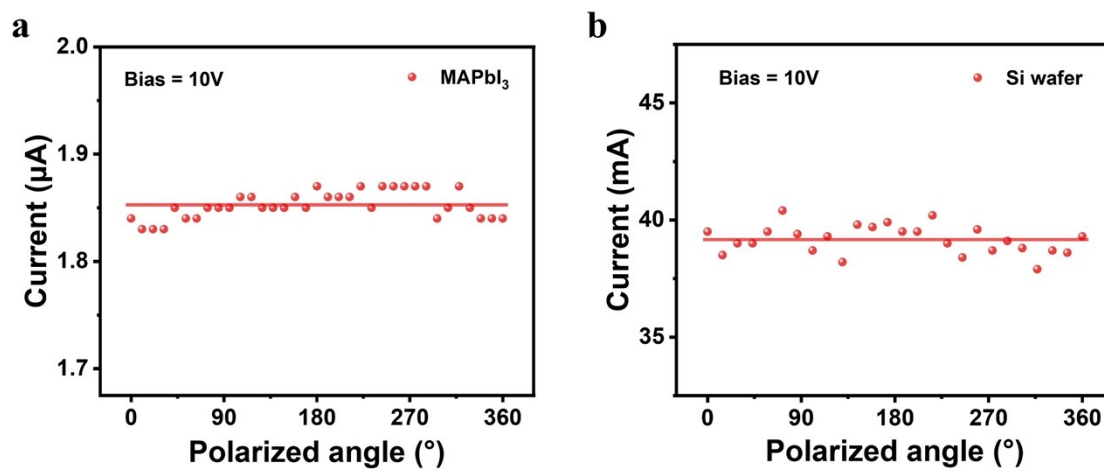


Figure S19. Polarized photocurrent of the pure (a) MAPbI₃ and (b) Si.

Table S1. Performance comparison of MAPbI₃/Si heterojunction NIR polarization-sensitive photodetector with other devices.

Devices	λ (nm)	D^* (Jones)	Polarized ratio	Condition	Ref.
MAPbI ₃ /Si	405-940	7.35×10^{12}	2.8 @ 940 nm 3.3 @ 785 nm	Self-powered	This work
MAPbI ₃ single crystal	275-790	-	-	1 V	1
MAPbI ₃ /graphene	260-900	4.5×10^{11}	-	Self-powered	2
MAPbI ₃ /PDPP3T	300-937	1.5×10^{10}	-	1 V	3
PTAA/MAPbI ₃ /C ₆₀ /BCP	350-800	7.8×10^{12}	-	0.1 V	4
MAPbI ₃ nanocrystal	400-980	1.77×10^{13}	-	Self-powered	5
MAPbI ₃ nanoribbon	300-800	8.21×10^{11}	1.44 @ white light	2 V	6
MAPbI ₃ nanowires	530	2×10^{13}	1.3 @ 530 nm	1 V	7
MAPbI ₃ needlecrystal	405	-	1.57 @ 405 nm	5 V	8
MAPbI ₃ nanowires	200-1000	4.73×10^{12}	2.2 @ 520 nm	1 V	9

References

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