Supplementary Information (SI) for ChemComm.
This journal is © The Royal Society of Chemistry 2026

PbS Quantum Dot Film as Hole Transport Layer for Self-Powered $AgBiS_2$ Nanocrystal Photodetectors

Jun Zhang, [a] Zhiyi Zhang, [a] Chen Ling, [a] Jianxian Zhou, [c] Yanping Lv, [b] Ming Yang, [b] Hao Wu, [a*] and Qichong Zhang [c*]

[a.] *School of Materials Science and Engineering, Shanxi Normal University, Taiyuan 030006, China. E-mail: fxcszx@163.com*

[b.] *School of Chemistry and Chemical Engineering, Shanxi Normal University, Taiyuan 030006, China.*

[c.] *Key Laboratory of Multifunctional Nanomaterials and Smart Systems, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China. E-mail: qczhang2016@sinano.ac.cn*

1. Experimental

1.1 Materials

Oleic acid, 1-Octadecene (ODE, 90%), Zinc acetate dihydrate (99.0%), 2-Methoxyethanol ($C_3H_8O_2$, ACS), Ethanolamine (C_2H_7NO, ≥99%), Silver acetate (Ag (OAc), ≥99.95%), Bismuth acetate (Bi $(OAc)_3$, ≥99.99%), Hexamethyldisilathiane (HMS, ≥97%), 3-Mercaptopropionic acid (MPA, ≥95%), 1,2-Ethanedithiol (EDT, ≥97%), Lead acetate trihydrate (≥99.99%), n-Butylamine ($C_4H_{11}N$, ≥99.7%) were purchased from Aladdin (Shanghai, China). The ITO coated glass substrates were purchased from Kaivo optoelectronic technology Co., Ltd (Zhuhai, China). Acetone, toluene, ethanol and n-octane were purchased from Kemiou chemical reagent Co., Ltd (Tianjin, China).

1.2 Synthesis of colloidal $AgBiS_2$ nanocrystals

The synthesis of $AgBiS_2$ nanocrystals was based on previous reports[1]. Briefly, 0.193 g $Bi(OAc)_3$, 0.0667 g of Ag(OAc) and 2.69 mL Oleic acid were put into a three-neck flask. This mixture was heated at 90 °C under vacuum for 7 h. After that, the atmosphere was switched to nitrogen, temperature was raised to 100 °C and held for 1 h. 106 μL HMS together with 2.5 mL ODE was quickly injected into the three-neck flask. The reaction solution quickly turned into dark brown. The heating was stopped and the reaction was allowed to cool naturally to room temperature. The nanocrystal solution was transferred to a centrifuge tube and precipitated with acetone, followed by centrifuged. Then it was dispersed in toluene, precipitated again with acetone for next centrifugation, and the precipitate was dispersed in n-octane with the concentration adjusted to 100 mg/mL.

1.3 Synthesis of colloidal PbS nanocrystals

The synthesis of PbS nanocrystals was based on previous reports[2]. Briefly, 0.3793 g lead acetate trihydrate, 0.786 mL oleic acid and 7.6 mL ODE were put into a three-necked flask. This mixture was heated at 100 °C under vacuum for 2 h. After that, 0.1 mL of HMS and 1 mL of ODE were mixed to prepare the sulfur precursor. Under nitrogen atmosphere, the sulfur precursor solution was quickly injected into the three-necked flask at 75 °C and the reaction was proceeded for 10 min. Then the heating source was removed and the reaction solution cooled naturally to room temperature. After that, the reaction solution was transferred into a centrifuge tube and precipitated with isopropanol, followed by centrifuged at 7000 rpm for 5 min. Then, the precipitate was dissolved in n-hexane and precipitated again with acetone. it was subsequently centrifuged at 4000 rpm for 5 min. Finally, the PbS nanocrystal precipitate was dissolved in n-hexane to prepare the solution with concentration of 20 mg/mL for further use.

1.4 Solution-Phase Ligand-Exchange for $AgBiS_2$ Nanocrystal Inks

1 mL 100 mg/mL $AgBiS_2$-OA nanocrystal solution was diluted with 9 mL of octane to get a 10 mL solution with

concentration of 10 mg/mL. 500 μL MPA was dissolved in 10 mL methanol to obtain the MPA ligand solution. Then the two solutions were mixed and stirred vigorously to promote ligand exchange. After stirring stopped, the two phases separated clearly. The upper octane phase was removed carefully, and the methanol phase was washed 3 times with 10 mL of octane. Then, 10 mL of toluene was added to the methanol phase, and the mixture was centrifuged at 3000 rpm for 5 min. The $AgBiS_2$-MPA precipitate was dried in a vacuum oven at room temperature for 20 min and stored in a glove box for further use[1].

1.5 Photodetectors Fabrication

The ITO-coated glass substrate was ultrasonically cleaned with acetone and ethanol successively, dried with nitrogen, and then treated with oxygen plasma. ZnO layer was prepared by sol-gel method. 1 g zinc acetate dehydrate was dissolved in 10 mL 2-Methoxyethanol and 284 μL ethanolamine[3]. The solution was spin-coated onto the ITO-coated glass substrate at 3,000 rpm and heated on a hot plate at 200 °C for 30 min. To ensure the uniform coverage of ZnO on ITO-coated glass substrate, this process was repeated once. Before depositing the $AgBiS_2$ layer, the ZnO layer was treated with oxygen plasma for 40 min. After that, the $AgBiS_2$-MPA nanocrystal powder was dissolved in a water/butylamine mixture (4:1 w/w) to prepare an ink with a concentration of 70 mg/mL. Then, the ink was filtered through a PTFE filter with a pore size of 0.22 μm and spin-coated onto the ZnO film layer at 2000 rpm for 60 s. Subsequently, the sample was transferred to a glove box, annealed at 115 °C for 10 min, and then stored for 48 h.

Preparation of PbS-EDT HTL: The PbS nanocrystal n-hexane solution with a concentration of 20 mg/mL was spin-coated onto the $AgBiS_2$ layer at 2500 rpm for 10 s. Then, the EDT acetonitrile solution (0.01 vol % in acetonitrile) was dropped onto the PbS film. After waiting for 30 s, it was subjected to spin-coating treatment at 2500 rpm for 10 s. After that, the PbS-EDT film was rinsed twice by spin-coating with acetonitrile. The above preparation process was conducted twice. When the spin-coating cycles of PbS-EDT were increased or decreased, the photovoltaic efficiency of $AgBiS_2$ nanocrystal solar cells declined rather than improved (Fig. S1). All of the above steps were carried out under ambient conditions. After that, the sample was transferred to a glove box and annealed at 70 °C for 10 min. Finally, the sample was transferred out of the glove box and stored in a desiccator for 12 h. The Au electrodes were evaporated onto the PbS-EDT HTL film through a shadow mask using an electron beam evaporation.

Preparation of Spiro-OMeTAD HTL: In the glove box, the Spiro-OMeTAD chlorobenzene solution was prepared according to previous reports[4]. After that, Spiro-OMeTAD chlorobenzene solution was spin-coated onto the ZnO/$AgBiS_2$ film surface at 3000 rpm for 30 s. The Au electrodes were evaporated onto the PbS-EDT HTL film

through a shadow mask using an electron beam evaporation. To investigate the effect of the hole transport layer on $AgBiS_2$ nanocrystal photodetectors, we fabricated ITO/ZnO/$AgBiS_2$/Au devices for comparison. The corresponding devices showed negligible photovoltaic performance (Fig. S2).

1.6 Measurement and characterization

The morphology was characterized by SEM (JSM-7500F), TEM (JEM-F200) and AFM (Bruker, Dimension Icon). The crystal structure was determined by XRD with Cu Kα1 radiation (λ=1.54056 Å) (Ultima IV-185). The chemical composition was analyzed by XPS (XPS, ES-CALAB 250Xi, Thermo Fisher Scientific). The Fermi level and valence band was detected by UPS (Specs UVLS, He I excitation, 21.21 eV). Absorbance spectrum measurement was performed via UV-vis-near IR spectrophotometer (UH4150, HITACHI). FT-IR spectrum was recorded using a Nicolet 8700 (Thermo Scientific). The EQE was measured using an EQE measurement system (EnliTech Taiwan). The current density-voltage (J–V) curve was measured under AM 1.5 G solar simulator (Sirius-SS150A-D, Zolix, 100 mW cm^{-2}) with a Keithley 2400 source meter. The photoelectric performance was measured at room temperature. The two electrodes of the photodetector were connected to a Keithley 2400 source meter, which was coupled with a wavelength-tunable light source (RS-323, NBeT instrument, Beijing, China) to investigate the photoelectric properties under different illumination conditions. Responsivity (R) is an important indicator for evaluating the performance of photodetectors, defined as $R=(I_{light}-I_{dark})/PS$, where I_{light} is the current under illumination, I_{dark} is the dark current, and P is the power of incident light in the effective area of the device, S is the effective working area[5].

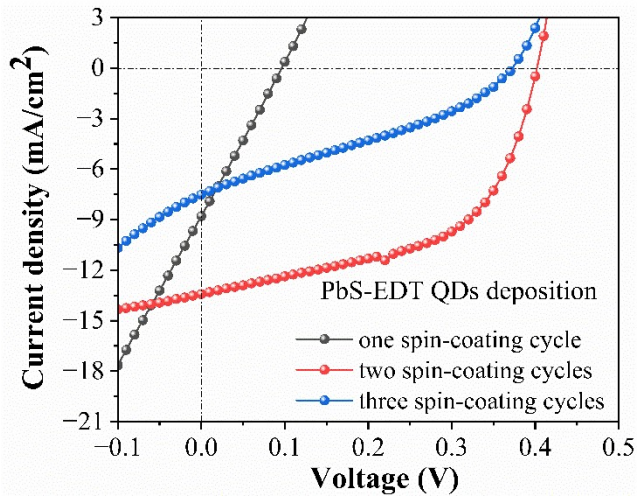

Fig. S1. J-V curves of $AgBiS_2$ nanocrystal photodetectors with different spin-coating cycles of PbS-EDT HTL under simulated AM1.5G illumination.

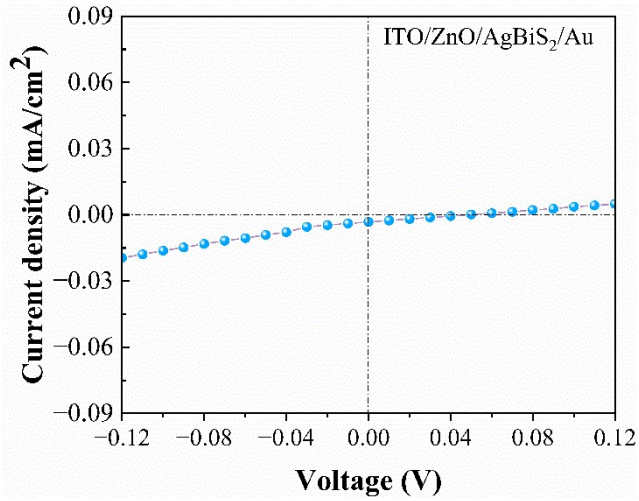

Fig. S2. J-V curves of $AgBiS_2$ nanocrystal photodetector without HTL under simulated AM1.5G illumination.

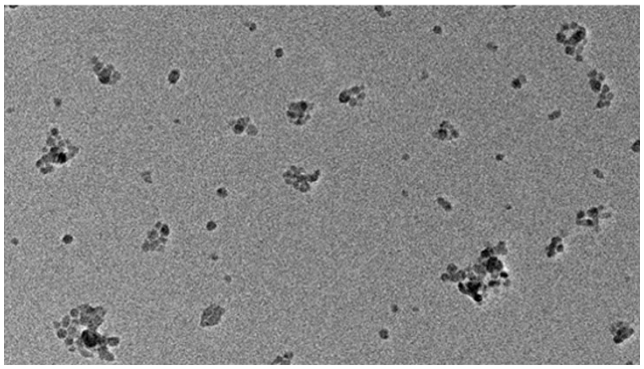

Fig. S3. TEM image of $AgBiS_2$ nanocrystals after the ligand exchanged from oleic acid to MPA.

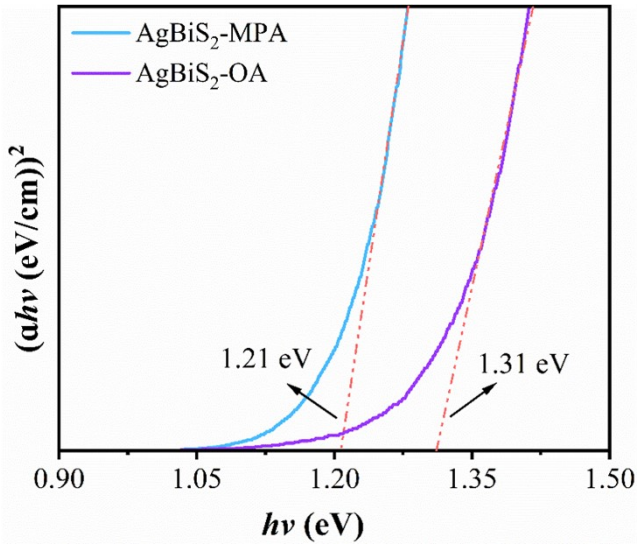

Fig. S4. The bandgaps of $AgBiS_2$ nanocrystals before and after ligand exchange.

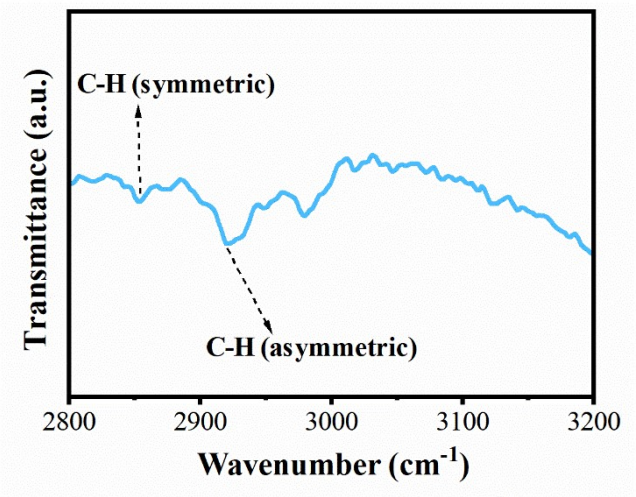

Fig. S5. Magnified FT-IR spectrum of MPA modified $AgBiS_2$ nanocrystals corresponding to the red frame in Fig. 1g.

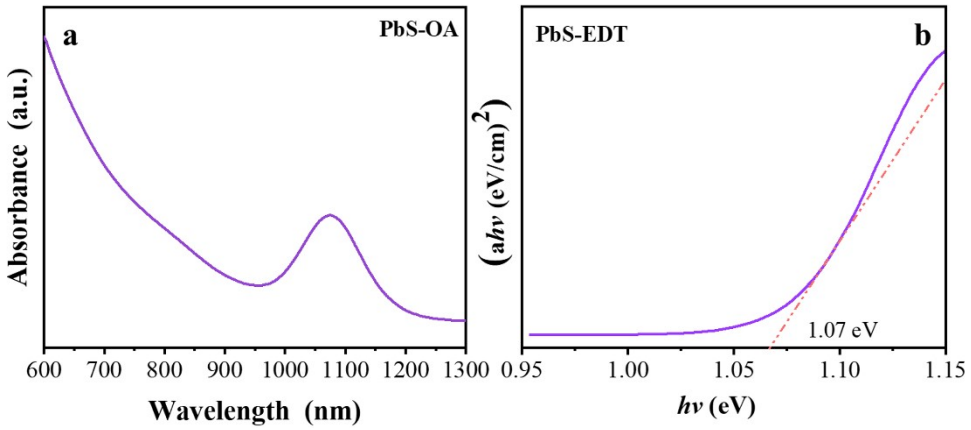

Fig. S6. (a) Absorption spectra of as-synthesized PbS quantum dots capped with oleic acid. (b) the band gap of PbS-EDT film.

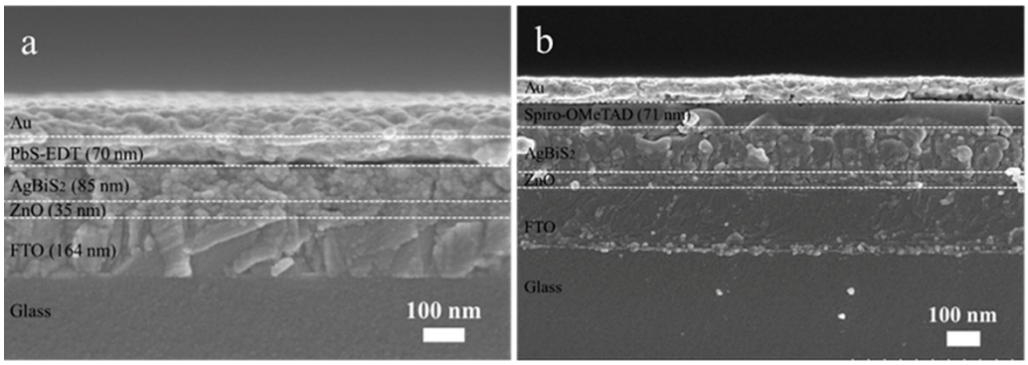

Fig. S7. SEM cross-sectional images of $AgBiS_2$ nanocrystal photodetectors with PbS-EDT HTL (a) and Spiro-OMeTAD HTL (b), respectively.

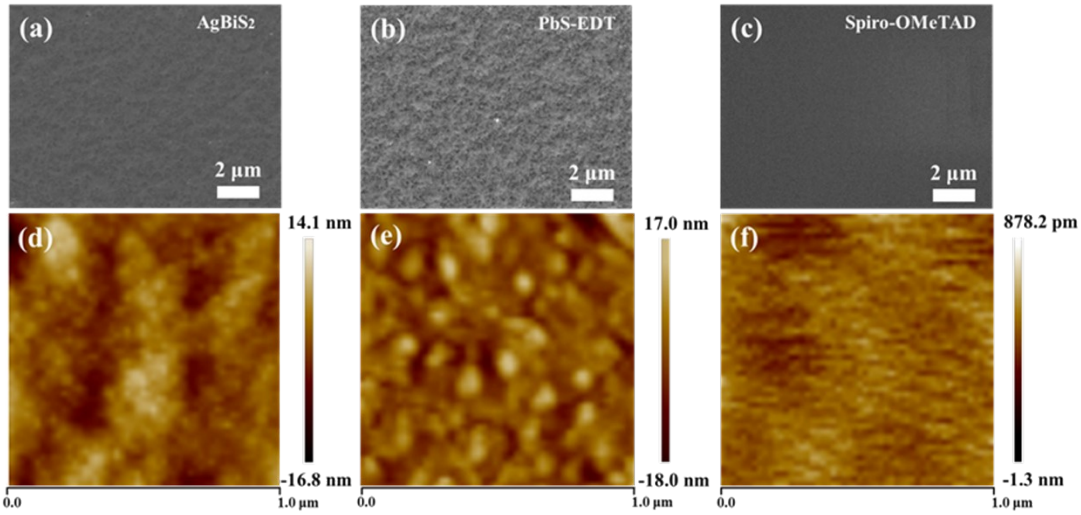

Fig. S8. SEM (a, b and c) and corresponding AFM (d, e and f) images of $AgBiS_2$, PbS-EDT and Sprio-OMeTAD fims, respectively.

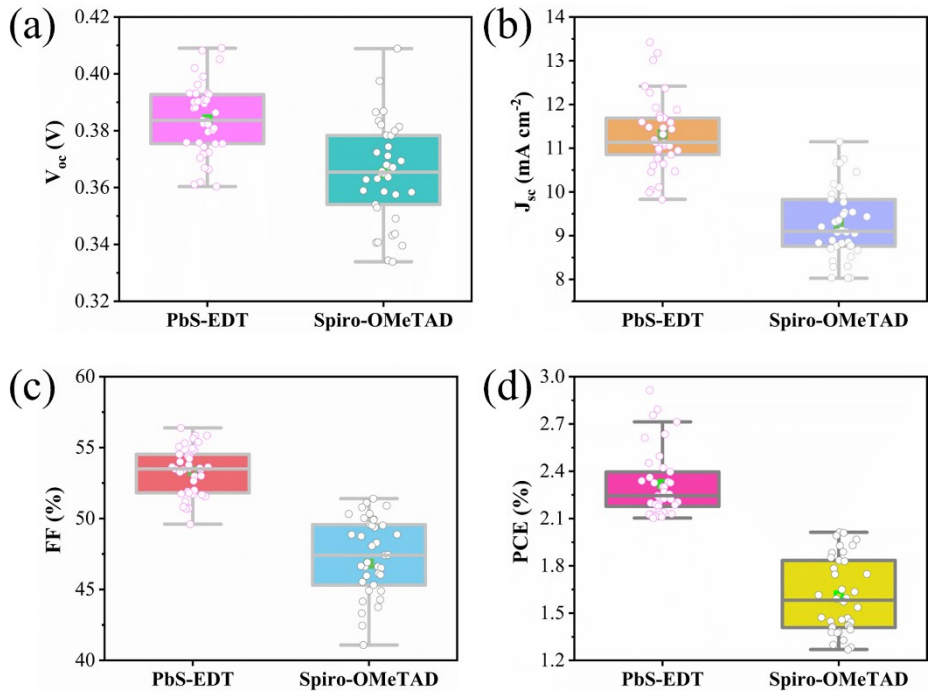

Fig. S9. Statistical distribution of V_{oc} (a), J_{sc} (b), FF (c) and PCE (d) for $AgBiS_2$ nanocrystal photodetectors with PbS-EDT and Spiro-OMeTAD as HTL.

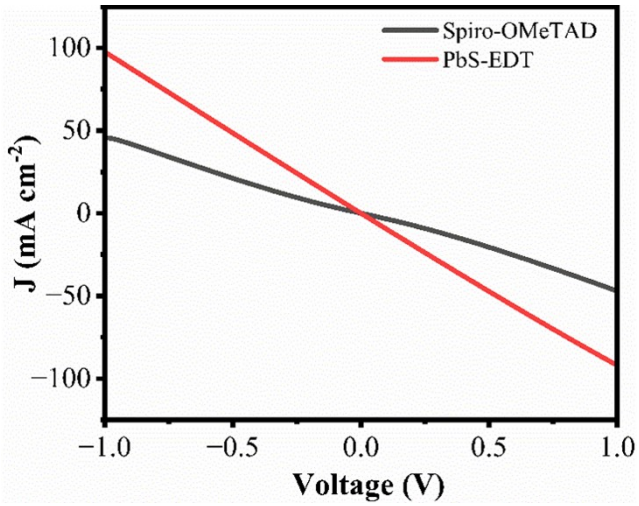

Fig. S10. Linear sweep voltammetry (LSV) curves of PbS-EDT and Sprio-OMeTAD films.

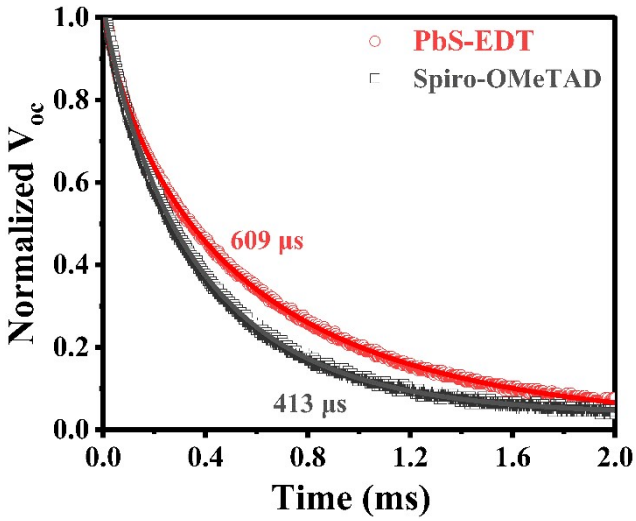

Fig. S11. TPV measurements of $AgBiS_2$ nanocrystal photodetectors with PbS-EDT and Spiro-OMeTAD as HTL.

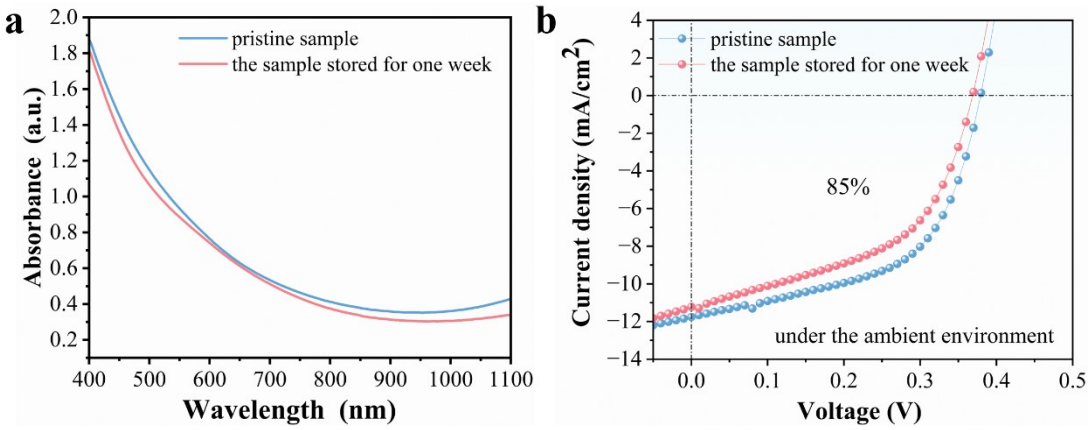

Fig. S12. Comparison of absorption (a) and J-V curves (b) between pristine $AgBiS_2$ nanocrystal photodetector and that stored in ambient environment for one week.

References

1. Y. Wang, L. Peng, Z. Wang and G. Konstantatos, *Advanced Energy Materials,* 2022, **12**, 2200700.
2. K. Lu, Y. Wang, Z. Liu, L. Han, G. Shi, H. Fang, J. Chen, X. Ye, S. Chen, F. Yang, A.G. Shulga, T. Wu, M. Gu, S. Zhou, J. Fan, M.A. Loi, W. Ma, *Advanced Materials*, 2018, **30**, 1707572.
3. M. Bernechea, N. Cates, G. Xercavins, D. So, A. Stavrinadis and G. Konstantatos, *Nature Photonics*, 2016, **10**, 521-525.
4. Y. Lv, Y. Shi, X. Song, J. Liu, M. Wang, S. Wang, Y. Feng, S. Jin, C. Hao, *ACS Applied Materials & Interfaces,* 2018, **10**, 31755-31764.
5. Z. Lu, L. Chen, J. Zhou, B. He, R. Liu, C. Zhu, P. Xue, Y. Sun, C. Li, L. Wei, Q. Li and Q. Zhang, ACS Nano, 2023, **17**, 20087–20097.