

Broad-spectrum (UV-Vis-Nir) high-performance photodetector based on
perovskite/quantum dot tandem heterostructure

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Experimental details

Materials: SnO₂ colloidal solution was purchased from Bolite. Methylammonium iodide (FAI), lead iodide (PbI₂), cesium iodide (CsI), and methylammonium chloride (MACl) were purchased from TCI, Sigma-Aldrich, and GreatCell Solar. All materials were used as received without further purification.

Perovskite precursor solution: The FA_{0.9}Cs_{0.1}PbI₃ perovskite precursor solution (1.4 M) was prepared by mixing FAI, CsI, and PbI₂ with 800 μL dimethylformamide (DMF) and 200 μL dimethyl sulfoxide (DMSO) in stoichiometric ratios. Subsequently, 7.2% PbI₂ and 5 mg/mL MACl were added to enhance crystallinity¹. The resulting precursor was vigorously shaken at room temperature for over 3 hours. Finally, the perovskite precursor solution was filtered through a 0.22 μm PTFE filter prior to use.

CQDs Synthesis and Ligand Exchange:: The thermal injection method² for synthesizing PbS quantum dots involved the following steps: Under a nitrogen atmosphere, 0.9 mmol PbCl₂, 3 mL OA, and 10 mL ODE were added to a 100 mL three-neck flask. The mixture was heated to 120°C and evacuated for 1 hour to remove moisture and low-boiling-point impurities. Subsequently, under nitrogen protection, the temperature was raised to 180°C, and the precursor solution prepared by dissolving 0.45 mmol TMS in 1 mL ODE was rapidly injected. After 30 seconds of reaction, immediately quench the reaction by immersing the flask in an ice-water bath. Upon cooling to room temperature, add 20 mL n-hexane and 20 mL acetone. Centrifuge (8000 rpm, 5 min) and discard the supernatant. Disperse the precipitate in n-hexane, then precipitate with isopropanol and wash three times. Finally, the purified PbS quantum

dots were dispersed in n-octane (approximately 50 mg/mL concentration) and stored in a nitrogen glovebox (O_2 and $H_2O < 0.1$ ppm) for later use. The ligand exchange process was conducted in the solution phase within the glovebox. The exchange solution was prepared by dissolving lead iodide (PbI_2 , 0.266 M), lead bromide ($PbBr_2$, 0.026 M), and cesium iodide (CsI , 0.013 M) in N,N-dimethylformamide (DMF). CQDs solution in octane (10 mg mL^{-1}) was added to the exchange solution at a 1:1 volume ratio. The mixed solution was vigorously shaken for 40 seconds until the CQDs completely transferred to the DMF phase. The DMF solution was then washed twice with octane. Following the exchange process, the CQDs were separated via centrifugation and subsequently subjected to vacuum drying^{3,4}.

Device Fabrication: Clean pre-patterned ITO-coated glass substrates ($10 \text{ } \Omega/\text{sq}$) by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropanol for 15 minutes each. Dry cleaned substrates under clean N_2 flow, then further dry overnight in a 60°C oven. Prior to depositing the electron transport layer, the substrate was exposed to an oxygen plasma cleaner for 5 minutes and immediately transferred to an N_2 glove box for later use. A SnO_2 colloidal solution (diluted 1:4 v/v with deionized water) was spin-coated onto the cleaned ITO substrate at 3,000 rpm for 30 seconds, followed by annealing at 150°C for 30 minutes. The ligand-exchanged PbS CQDs were redispersed in a mixed solvent of butylamine (BTA) and DMF (4:1 v/v) to achieve a concentration of 320 mg mL^{-1} . The resulting ink was deposited via spin-coating at 2500 rpm for 40 s, yielding a film thickness of approximately 250 nm. Subsequently, an annealing treatment was performed to remove residual solvents⁴. Next, $70 \text{ } \mu\text{L}$ of the

perovskite precursor solution was spin-coated onto the top of the PbS layer at 4,000 rpm for 40 seconds. After 20 seconds, 200 μL of chlorobenzene was dropped onto the film, followed by annealing the corresponding film at 150°C for 20 minutes in air ⁵. Finally, the Au electrode (80 nm) was thermally evaporated at a rate of 0.05 nm s^{-1} under a vacuum of 4×10^{-4} Torr. The Au electrode was deposited by thermal evaporation through a shadow mask featuring an opening of $15 \text{ mm} \times 40 \mu\text{m}$, centered on the ITO pixel. The resulting overlap area is approximately $A = 0.006 \text{ cm}^2$, accounting for slight mask alignment tolerances. This area was consistently used for all responsivity (R) and specific detectivity (D^*) calculations throughout the manuscript. Note that all device fabrication procedures were performed in a nitrogen glovebox (O_2 and $\text{H}_2\text{O} < 0.1 \text{ ppm}$).

Supplementary Figures

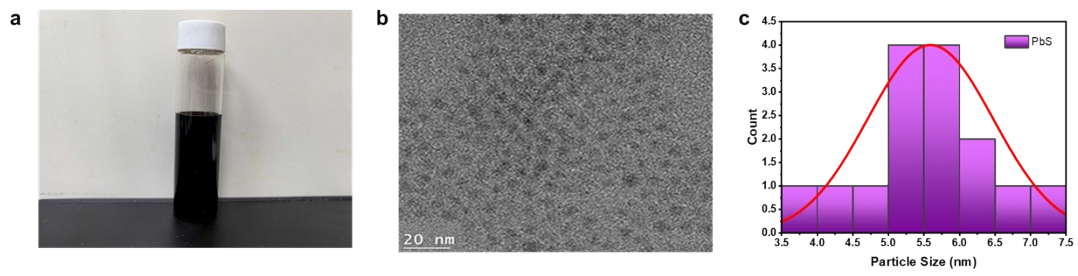


Figure S1. Morphology and particle size analysis of PbS quantum dot samples.

a) Photograph of PbS CQDs solution. b) TEM image of PbS CQDs. c) Particle size analysis of PbS CQDs.

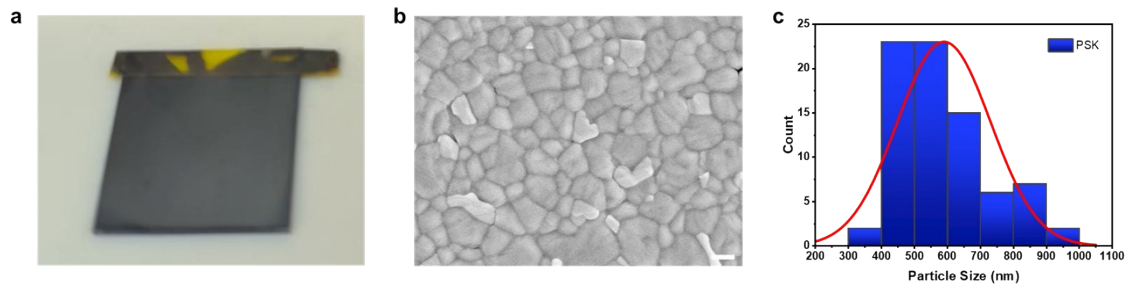


Figure S2. Optical morphology and grain size analysis of PSK films.

a) Photograph of PSK film. b) SEM image of PSK film. (scale bar: 400 nm) c) Grain size analysis of PSK film by SEM

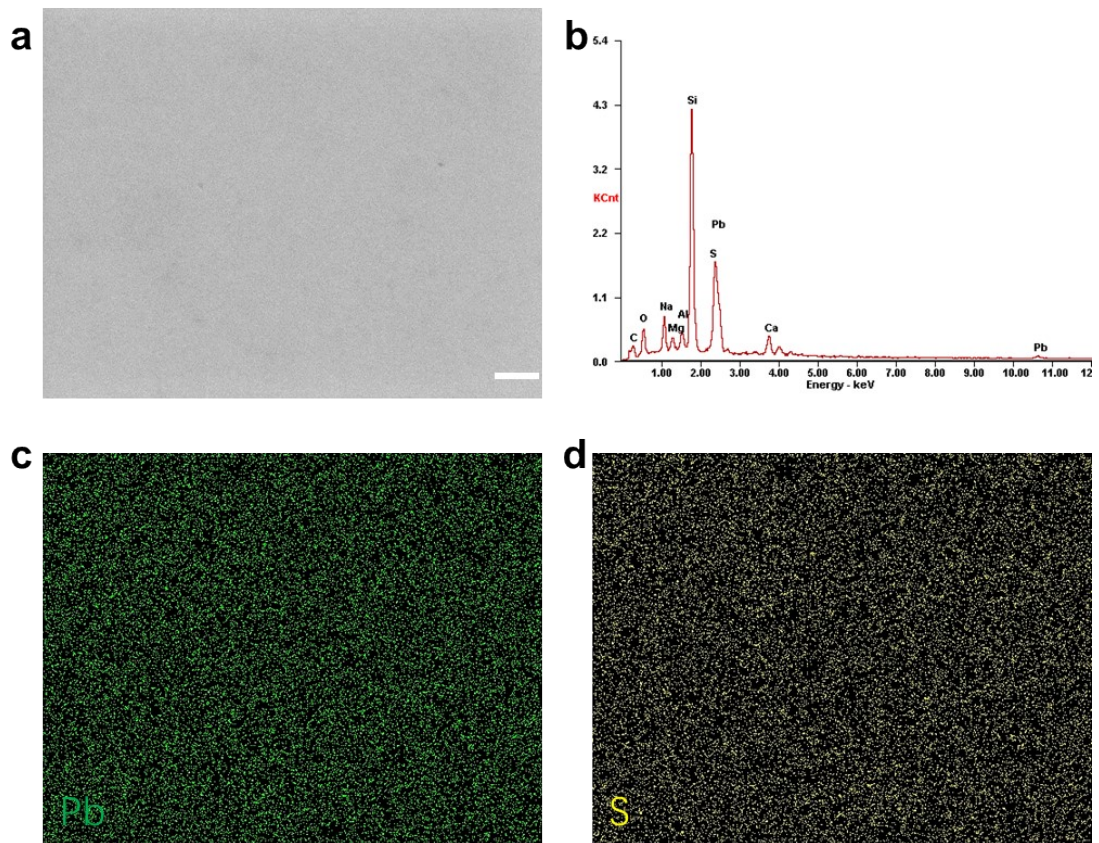


Figure S3 EDS Analysis of PbS Thin Films.

a) SEM top view of PbS thin film. Scale bar: 1 μm . b) EDS spectrum of PbS thin film.

c-d) Distribution of Pb and S in EDS mapping of PbS thin film

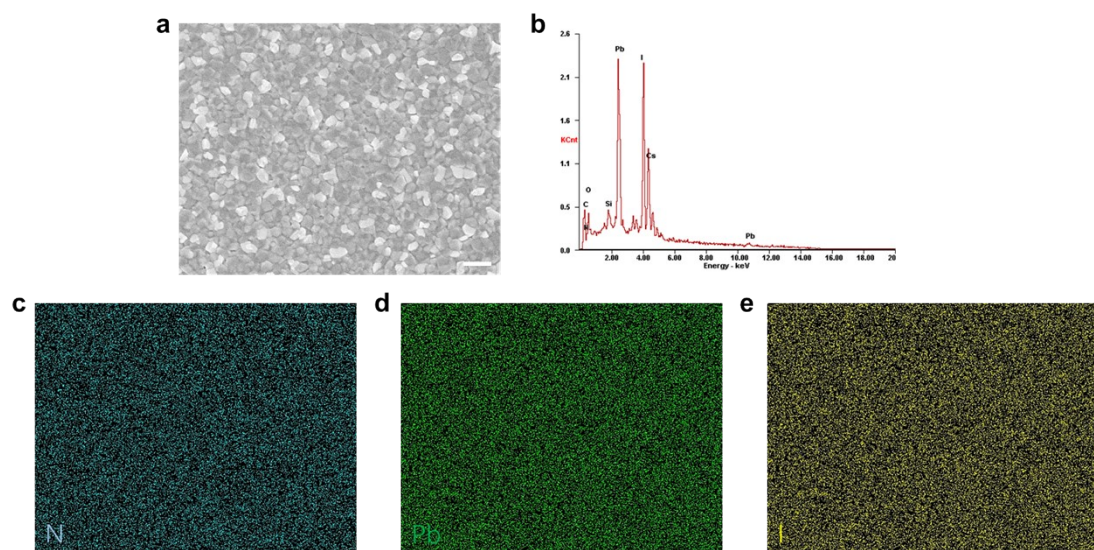


Figure S4 EDS analysis of PSK thin film.

a) SEM top view of PSK thin film (scale bar 1 μm). b) EDS spectrum of PSK thin film.

c–e) Distribution of N, Pb, and I in PSK EDS mapping.

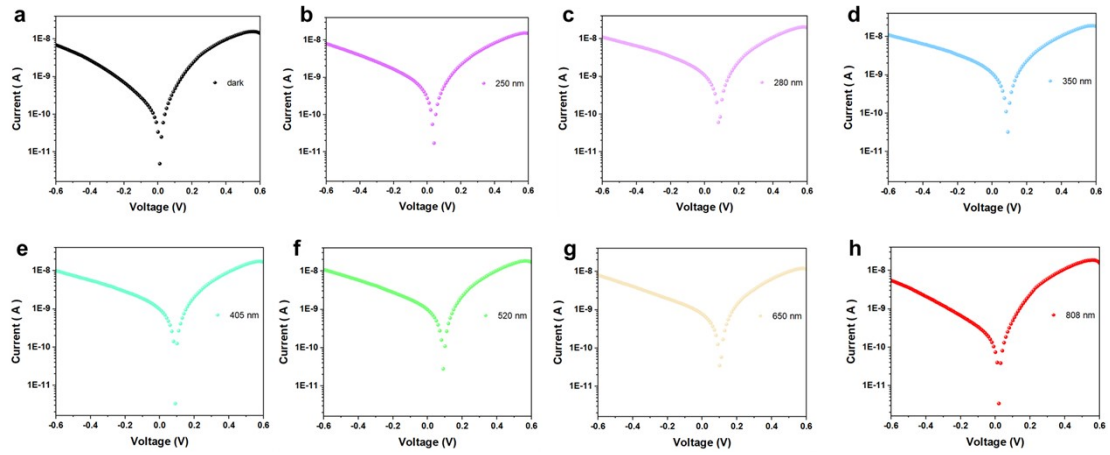


Figure S5 I-V curves of PSK/PbS composite samples under illumination of different wavelengths. a) Dark. b) 250 nm. c) 280 nm. d) 350 nm. e) 405 nm. f) 520 nm. g) 650 nm. h) 808 nm.

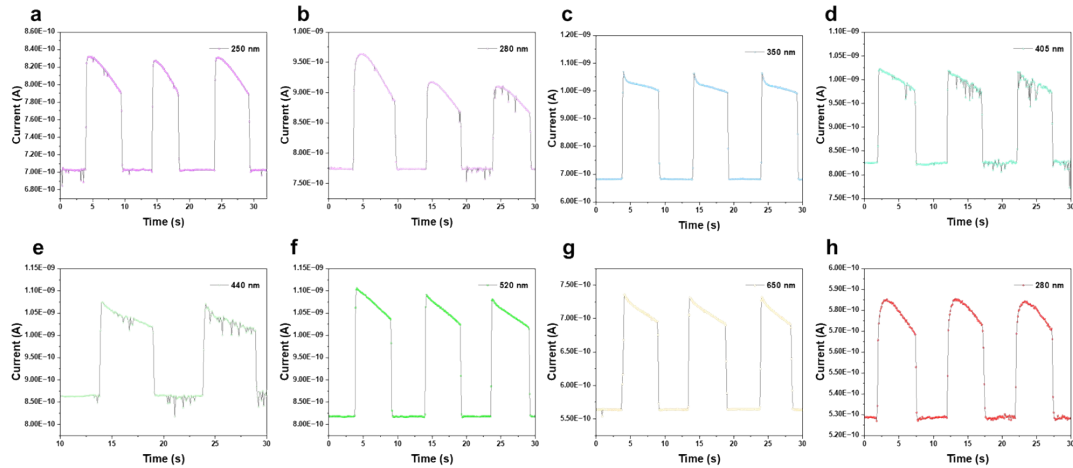


Figure S6 I-t response curves of PSK/PbS composite samples under illumination at different wavelengths. a) 250 nm. b) 350 nm. c) 405 nm. d) 440 nm. e) 520 nm. f) 650 nm. g) 808 nm. h) 1550 nm.

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