Supporting information

Charge carrier management via semiconducting matrix for efficient self-powered quantum dot infrared photodetectors

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1. Experimental section

1.1 Chemicals and Reagents

Lead iodide (PbI₂, >99.5%), Lead oxide (PbO, >99.9%) and Oleic acid (OA, >99%), N, N-dimethylformamide (DMF, \geq 99.9%), 1-Octadecene (ODE, \geq 90.0%), 3-Mercaptopropionic acid (MPA, >98%), Copper thiocyanate (CuSCN, >99%), n-Butylamine (BTA, \geq 99.5%), Toluene (\geq 99.5%) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. Acetone (>99.5%) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Methanol (MeOH, 99.9%) was purchased from Adamas-beta. Tin (IV) oxide (SnO₂, 15% in H₂O colloidal dispersion) was purchased from Alfa Aesar. Conductive carbon paste (DD-10, containing carbon black and graphite powder) was purchased from Guangzhou Sadie Technology Development Co. Ltd. ITO glass substrates were purchased from Shangyang Technology. Noted that all chemicals and reagents were used as received without further purification.

1.2 Synthesis of PbS QD

The mixture of PbO (0.9 g), OA (3 mL) and ODE (36 mL) were placed into a three-neck flask and then degassed at 60 °C for 15 min. Following, the mixture was quickly heated to 140 °C and continued to stir for 1 h under N₂ atmosphere. After that, the temperature of the three-neck flask was cooled to 100 °C and then a mixture solution of 420 μ L of trimethylsilyl iodide and 18 mL of ODE was quickly injected into the flask. After 60 s, the three-neck flask was rapidly cooled in an ice bath to quench the reaction. Next, the crude PbS QD was obtained by adding some amount of acetone into the three-neck flask. Subsequently, the crude PbS QD was centrifuged at 6000 and the precipitated PbS QD was redispersed into toluene. Finally, the precipitation and centrifugation of the crude PbS QD with methanol was repeated for 3 times. The obtained OA-PbS QD was dispersed in octane at concentration of 50 mg/mL for use.

1.3 Preparation of PbS QD Ink

The PbI₂-capped PbS QD was prepared through a ligand exchange process in ambient air. First, halide precursor solution for ligand exchange was prepared by dissolving PbI₂ (0.14 M) and NH₄Ac (0.06 M) in 16 mL of DMF and stirring for two hours. Then, 3 mL of OA-PbS QDs (17 mg/mL) was mixed with 2 mL of the halide precursor solution. After vigorously shaking the mixture for 1.5 minutes, allow it to stand until the solution separates, and then remove the clear supernatant. The PbI₂-PbS QDs are precipitated from the DMF using toluene. Precisely weigh the obtained PbI₂-PbS QDs and then, 0.25 mg of CuSCN was dissolved in 10 mL of BTA. After complete dissolution, a light blue transparent solution was obtained. Using BTA and BTA (CuSCN) redisperse the previously accurately weighed PbI_2 -PbS QDs at a concentration of 200 mg/mL to prepare the PbS QD ink for future use.

1.4 Device fabrication

The preparation for the SnO₂ precursor solution involves diluting the commercial SnO₂ solution at a volume ratio of SnO₂: deionized water of 1:4. Before preparing the SnO₂ ETL, the diluted solution is filtered using a 0.22µm PTFE filter. The SnO₂ film was prepared by spin-coating SnO₂ dispersion solution upon the ITO substrate at 4000 rpm for 30 s and undergoing thermal annealing at 150 °C for 30 min. The PbS QD ink was spin-coated on the ITO/SnO₂ substrate at 2500 rpm for 60 s to obtain PbS QD active layer with a thickness of approximately 200 nm. On top of the PbS QD film, two layers of OA-PbS QD films as the p-type hole transport layer was obtained by spin-coating 10 vol% MPA (named p-PbS). The carbon paste (commerlized DD-10 from Saidi Technique, containing carbon black and graphite powder) was blade-coated on the plastic tape patterned substrate, forming a wet film thickness of about 150 µm. The wet film was annealed at 110°C for 5 minutes to finish the fabrication of photodetectors.

1.5 Device characterization

The transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) were performed on the JEM-F200 (JEOL, Japan). The UV-Vis absorption spectra were recorded with an ultraviolet-visible spectrophotometer (Cary 5000, Varian, USA). Steady-state photoluminescence (PL) was performed using a fluorescence spectrophotometer (FLS1000, Edinburgh Instruments, the United Kingdom) with an

excitation wavelength of 600 nm. The two films were prepared under the same concentration of quantum dots to ensure similar film thickness. The Current densityvoltage (J-V) characteristics (photo current and dark current) was measured using a Keithley 2400 source meter and a sunlight simulator (Crown technology, USA). External quantum efficiency (EQE) and current-wavelength spectra were obtained by a EQE measurement system (Test Station 500ADX, Crown Technology, USA). The photoelectronic and application characteristics of PDs were carried out on an electrochemical workstation (CHI-660E, Chenhua Inc., China) and monochromatic light at a wavelength of 808 nm (VCL-808nmM1-4.0W, Beijing Blue-print Photoelectric Technology Co., Ltd., China). During this process, a neutral density filter (NDFR-25C-4, LBTEK, China) was installed in front of the laser emission port to achieve the desired light power density and a radiometer (DLY-1810C, DELIXI ELECTRIC, China) was employed to calibrate the optical power for each usage. The laser's on-off cycle is set to 10 s, and the photodetector operates for at least five cycles at each light intensity and the average values of current obtained within these five cycles serve as the basis for calculating R, D and other relevant parameters. The transient photocurrent (TPC) measurements were test was conducted on a measurement system comprising a digital oscilloscope (Keysight Technologies DSOS104A) and a 532nm laser (Innolas spitlight 100). By simply setting the system resistance to 20Ω , it simulates a near-short-circuit condition. EIS test was performed on the same electrochemical workstation with that for PD measurements, under dark condition and different bias with a frequency range from 1 MHz to 100 Hz. To determine the area of the carbon

electrode, vernier caliper (DVC-S1, DELIXI ELECTRIC, China) was used to measure the length and width of the electrode separately. Each electrode is measured at least three times, and then the average value is calculated.

2. Results and discussion



Figure S1. Statistical results of electron mobility



Figure S2. Tauc plot of PbS-QD film.



Figure S3. a) Detectivity and b) Responsivity of photodetectors based on different concentration of CuSCN.



Figure S4. J-V curve of Target- and Control photodetectors obtained under AM 1.5G illumination.



Figure S5. The Nyquist plots of a) control photodetector and b) target photodetector.



Figure S6. The recombination resistance (R_{rec}) of control- and target photodetector obtained from Nyquist plots of devices under different bias voltage.



Figure S7. Equivalent circuit used for Nyquist plots fitting

Table S1. Different resistances extracted from Nyquist plots of devices.

Photodetectors	$R_{s}\left(\Omega ight)$	$R_{tr}\left(\Omega ight)$	$R_{rec}\left(\Omega ight)$
Control devices	45	615	1295
Target devices	50	617	3277