Supporting Information

Metal Chalcogenide Complexes Ligands Enhanced Response

in Hybrid Graphene/PbS Quantum Dots Photodetector

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CHARACTERIZATION



Figure S1. Raman spectrum of monolayer graphene and graphene/PbS-MCC QDs films on SiO₂. The characteristic Raman peaks can be seen, peak G at 1590 cm⁻¹ showing the sp² bond, and 2D peak at 2696 cm⁻¹ showing the double resonance process of the two phonons. The G peak and the 2D peak exhibit weak redshift in the Raman spectra after the deposition of PbS-MCC QDs. The redshift of G peak indicates the p-type doping effect induced by the charge transfer (holes) from PbS-MCC QDs to graphene in the hybrid structure.¹



Figure S2. Representative HRTEM image of the synthesized PbS-OA QDs. PbS-OA QDs with dimensions of (a) 3 nm, (b) 4 nm, (c) 5 nm and (d) 6 nm respectively. High-resolution transmission electron microscopy provides detailed information on the synthesized OA-capped QDs with high quality. The PbS-OA QDs are uniform. The size of the quantum dots shows a similar variation to the absorption spectrum.²



Figure S3. Representative HRTEM image of the $(NH_4)_3AsS_3$ (MCC) ligand exchange PbS QDs. (a) 5 nm PbS-MCC QDs, and (b) 6 nm PbS-MCC QDs. Because the chain of inorganic ligands is too short, the PbS QDs will have agglomeration phenomenon. The average size of these QDs is estimated to be approximately (a) 5 nm and (b) 6 nm demonstrating similar changes in their absorption spectra.³



Figure S4. Scanning electron microscopy (SEM) images of PbS QDs ligand-exchanged with $(NH_4)_3AsS_3$ (MCC) ligands. Figures (a) and (b) depict the 5 nm PbS-MCC QDs and 6 nm PbS-MCC QDs, respectively. PbS-MCC QDs form films through spin-coating, and the image indicates that the resulting film is relatively uniform.⁴



Figure S5. Surface atomic force microscopy (AFM) characterization images of PbS QDs after ligand exchange with MCC ligands. (a) shows the 5 nm PbS-MCC QDs, while (b) displays the 6 nm PbS-MCC QDs. The film thickness of the PbS-MCC QDs is approximately 150 nm.⁵



Figure S6. Transient absorption spectra (TAS) mapping of PbS-MCC QDs. (a) presents the TAS diagram of a 6 nm PbS-MCC QDs/graphene device excited with a 1700 nm laser in the visible range, while (c) shows the excitation wavelength at 1800 nm in the near-infrared range. The TAS diagrams for the 5 nm PbS-MCC QDs/graphene device, excited by a 1700 nm laser in the visible range, are shown in (b), and for the 1800 nm laser in the near-infrared range in (d). The red area represents signal of exciton bleaching, and the exciton bleaching region corresponds to the absorption peak in their absorption spectrum.⁶



Figure S7. Relaxation curves for 5 nm PbS-MCC QDs at a pump fluence of 0.1 mJ cm⁻², with probe pulses at 896 nm, 976 nm, 1093 nm, and 1167 nm, respectively. The lifetime formula is $\tau ave = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$. The fitting curve reveals that the 1034 ps are shown when probing at 1167 nm. This implies charge transfer from QDs to graphene due to the presence of fewer sub-bandgap trap states and reduced carrier recombination.⁷



Figure S8. The MCC ligand-exchanged PbS QDs/ ethanol solution (50 mg/mL) was spin coated on the electrode.⁸



Figure S9. Experimental illustration of fabrication of PbS QDs thin film on graphene. An Ultraviolet Maskless Lithography machine was used to achieve the patterned electrodes. The fabricated electrodes were then cleaned using ultrasonic in acetone, n-hexane and DI water were used step by step to achieve a clean top surface. The QDs were using spin-coating before the film fabrication.⁹



Figure S10. Optical microscope of PbS-MCC QDs and patterns of the electrodes. The active channel width and length are 4 μ m and 4 μ m, respectively. All of the active channels and source/drain electrodes are patterned using Ultraviolet Maskless Lithography machine.¹⁰



Figure S11. Graphene/MCC-QDs stability test within 144 hours. The data indicates that the devices maintain relatively stable performance over this period, with only minor fluctuations in responsivity and detectivity.



Figure S12. Band alignment between PbS QDs and graphene before and after ligand exchange. The bandgap of PbS QDs decreases after ligand exchange. The smaller bandgap likely induces a more favorable band alignment between PbS QDs and graphene post-ligand exchange. Thus, lowering the energy barrier for charge transfer. This optimized alignment enhances the separation and transport of photogenerated carriers, ultimately boosting both the responsivity and detectivity of the photodetector.

Photodetector	Responsivity	detectivity	$ au_{ave}$
	(A/W)	(Jones)	
Graphene/MAI-			
PbS QDs	453.9	108	28.8 ps
Graphene/MAI/			
TBAI-PbS QDs	986.7	108	46.1 ps
Graphene/MAI/			
TBAI/EDT-PbS	6.7×10^{3}	109	247.1 ps
QDs			
This work	1.82×10^{4}	1012	1.03 ns

Table 1. Photodetector performance of QDs with different ligands

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