Supporting Information

Near Infrared-II Photodetectors Based on Silver Selenide Quantum Dots on Mesoporous TiO_2 Scaffolds

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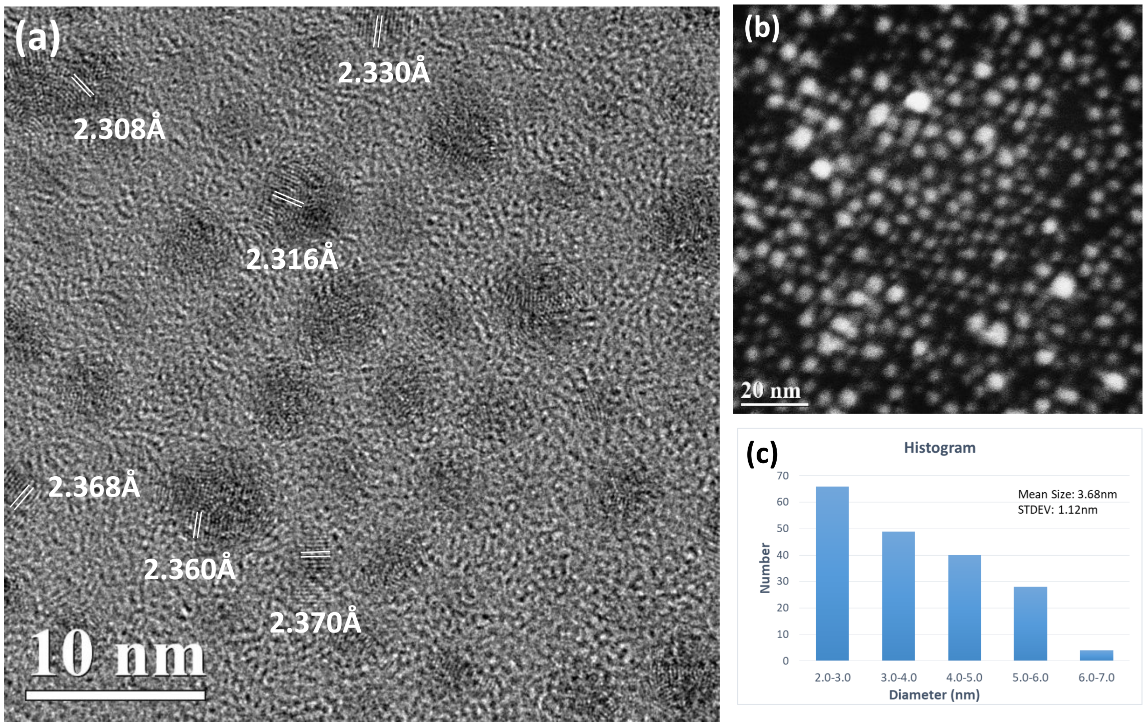
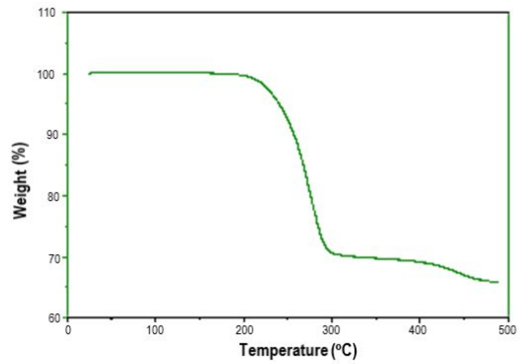


Figure S1. *Size and size distribution of Ag_2Se QDs. (a) High resolution TEM image (scale bar = 10 nm). Several d-spacings are labelled. (b) High angle annular dark field TEM image (scale bar = 20 nm). (c) Histogram of Ag_2Se sample corresponding to (b), with a mean diameter of 3.68 nm and a standard deviation of 1.12 nm (total measured QD number = 187).*

(a) EDX results

Spectrum	P	S	Se	Ag
Spectrum 1	0.06	17.13	20.64	62.17
Spectrum 2	1.25	18.20	20.25	60.30
Spectrum 3	-0.16	18.05	19.48	62.63
Mean	0.38	17.79	20.12	61.70
Std. deviation	0.76	0.58	0.59	1.24
Max.	1.25	18.20	20.64	62.63
Min.	-0.16	17.13	19.48	60.30

(b) TGA



(c) Ligand (1-dodecanethiol, DDT) density calculation

For one DDT-capped Ag_2Se QD with a mean diameter of 3.7 nm (radius r = 1.85 nm), its volume (Vol, perfect sphere is assumed) is calculated to be:

$$\text{Vol} = 4\pi r^3/3 = 8.44\pi\ (\text{nm})^3 \qquad (S_1)$$

The crystal weight (W, ligand free) is calculated to be:

$$W = \text{Vol x density} = 8.44\pi \text{ x } 10^{-21}\ (\text{cm})^3 \text{ x } 8.216\ (\text{g cm}^{-3}) = 6.93\pi \text{ x } 10^{-20} \text{ g} \qquad (S_2)$$

(*The density of bulk orthorhombic Ag_2Se is used because that of tetragonal phase is not available*)

According to TGA results in (b), weight of DDT (W_{DDT}) is ~30% of total weight,

$$W_{DDT} = 6.93\pi \text{ x } 10^{-20} \text{ g x } (30/70) = 2.97\pi \text{ x } 10^{-20} \text{ g} \qquad (S_3)$$

Since DDT molecular weight is 202.4 g·mol^{-1}, the number of DDT ligand (N_{DDT}) is calculated to be:

$$N_{DDT} = N_A \text{ X } (2.97\pi \text{ x } 10^{-20}/201.4) = 88.81\pi \qquad (S_4)$$

Where N_A is Avogadro constant, 6.022 X 10^{23} mol^{-1}.

So Ligand density ρ is calculated to be:

$$\rho = N_{DDT}/\text{surface area} = 88.81\pi/(4\pi r^2\ \text{nm}^2) = 6.49\ \text{nm}^{-2} \qquad (S_5)$$

Scheme S1. *(a) Energy dispersive x-ray spectroscopy tabulated results; (b) Thermal gravimetric analysis (TGA) spectrum. The spectrum was collected with 4.4 mg purified Ag_2Se QDs at a heating rate of 10 ^oC/min in N_2 (TA Instruments TGA 2050 CE); (c) Calculation of ligand density on Ag_2Se QD surface.*

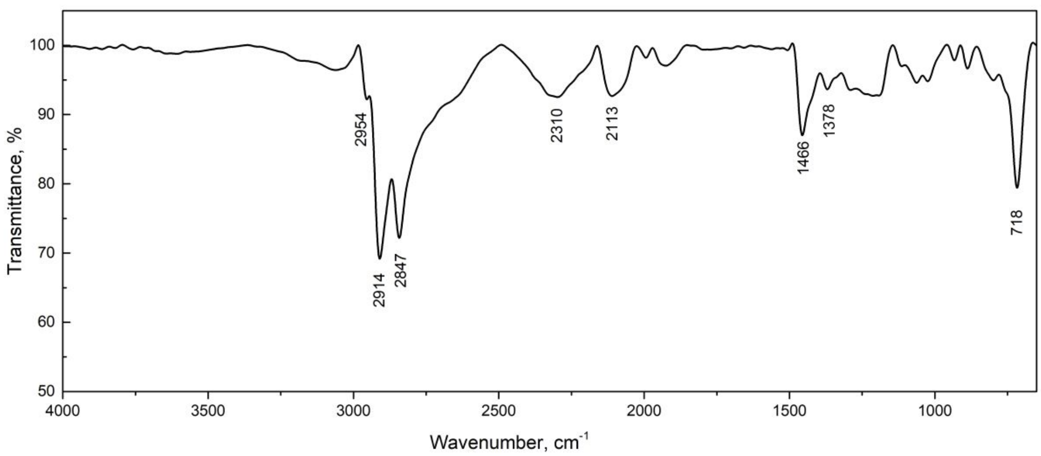


Figure S2. *Fourier Transform Infrared (FTIR) spectrum of the purified Ag_2Se nanocrystals (acquired on Cary 630 with 2 cm^{-1} resolution and an average of 64 scans). The peaks at 2954 cm^{-1}, 2914 cm^{-1}, and 2847 cm^{-1} are assigned to the stretching vibrations of CH_2 and CH_3 in the alkane chain, and the peaks at 1466 cm^{-1} and 1378 cm^{-1} are the bending vibrations of CH_2 and C-CH_3, respectively.[1,2] The peak at 718 cm^{-1} is ascribed to the stretching vibration of CH_2-S.[2]*

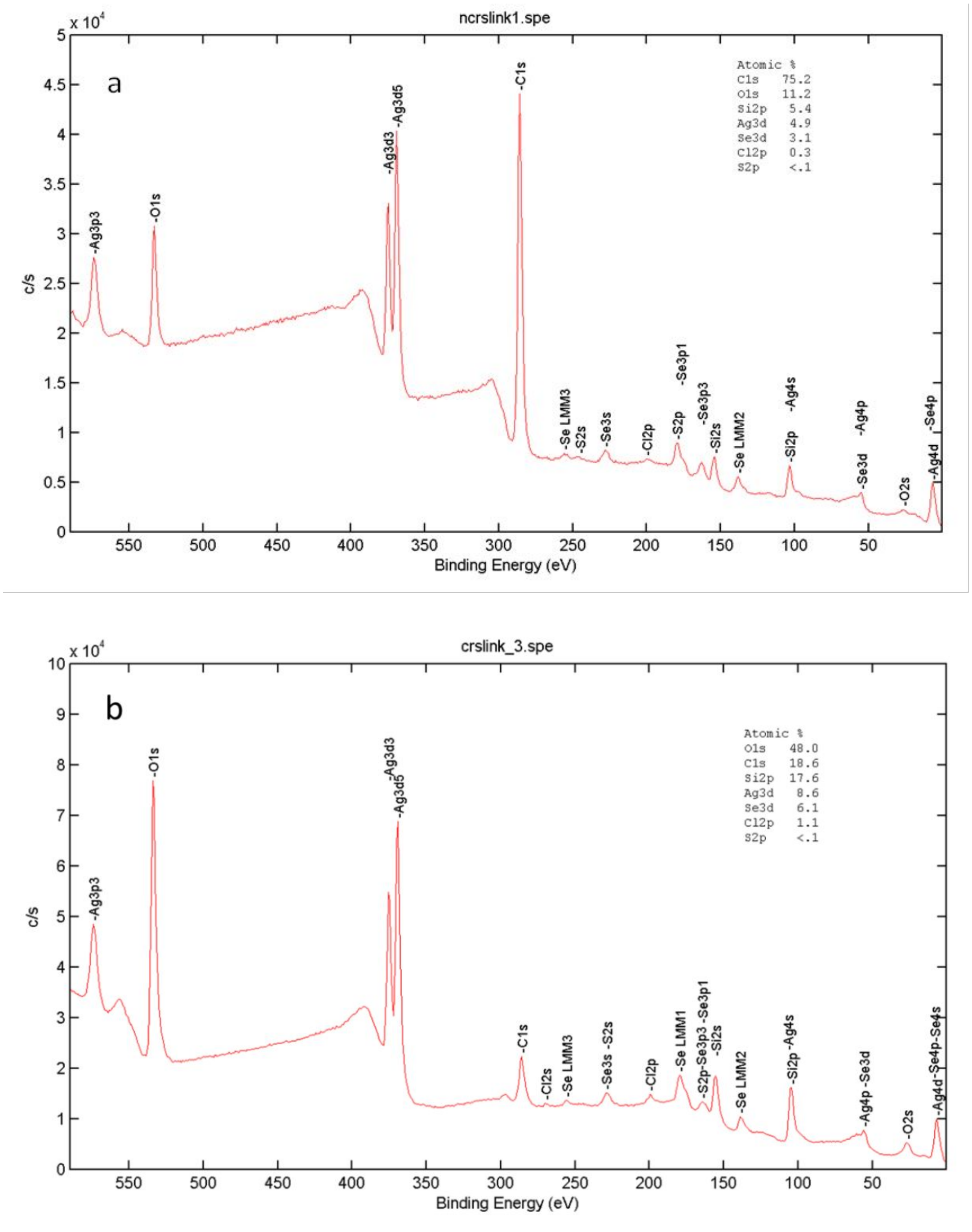


Figure S3. *XPS spectra of Ag_2Se QDs on Si wafers before (a) and after (b) ligand exchange with BDT.*

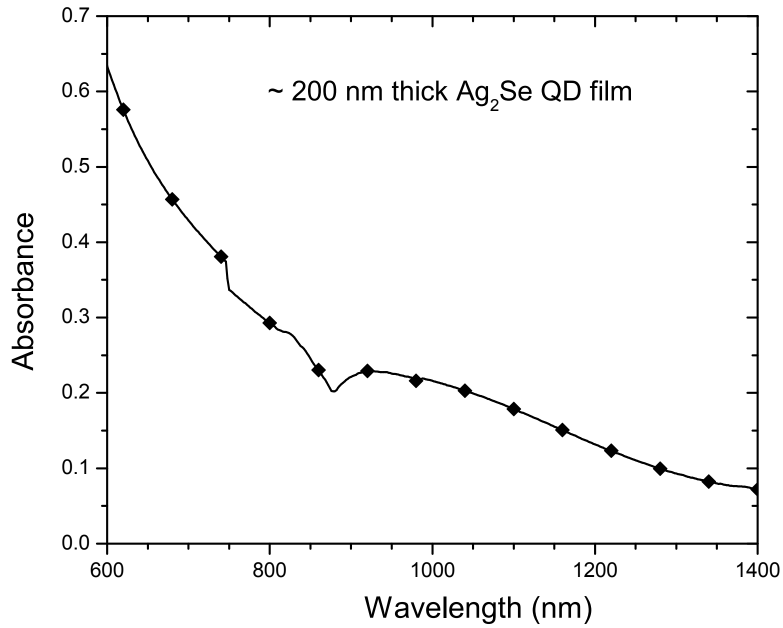


Figure S4. *Absorption spectrum of an Ag_2Se QD film on quartz fabricated by a layer-by-layer process using BDT as a crosslinker. Note that the absorption features at lower wavelengths (700-900 nm) are due to the equipment.*

References

( ) Shi, L.-J.; Zhu, C.-N.; He, H.; Zhu, D.-L.; Zhang, Z.-L.; Pang, D.-W.; Tian, Z.-Q. Near-infrared Ag_2Se Quantum Dots with Distinct Absorption Features and High Fluorescence Quantum Yields. *RSC Adv.* **2016**, *6*, 38183–38186.

(2) Chakraborty, I.; Moulik, S. P. On PbS Nanoparticles Formed in the Compartments of Water/AOT/n-Heptane Microemulsion. *J. Nanopart. Res.* **2005**, *7*, 237–247.