Supporting Information

Effective surface passivation of environment-friendly colloidal quantum dots for highly efficient near-infrared photodetectors

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Materials: Copper(I) iodide (CuI) (≥99.99%), Indium acetate $In(Ac)_3$ (≥99.99%), Tin(II) chloride ($SnCl_2$) (reagent grade, 98%), selenium (Se), Zinc stearate, Oleylamine (OLA) (technical grade, 70%), diphenylphosphine (DPP), 1-octadecene (ODE) (technical grade, 90%), Trioctylphosphine (TOP) (97%), Hexadecyltrimethylammonium bromide (CTAB), zinc acetate dihydrate ($Zn(Ac)_2{\cdot}2H_2O$), Sodium sulfide (Na_2S), Sodium sulfite (Na_2SO_3), Hexane, Toluene, Methanol, Ethanol, Acetone were bought from Sigma-Aldrich Inc. Titania 18NR-AO paste was purchased from Dyesol (Queanbeyan, Australia). The Ti-Nanoxide BL/SC solution was purchased from Solaronix. All chemicals were used without further purification.

Synthesis of CISnSe core QDs: The CISnSe QDs were synthesized via a hot injection technique, in brief 0.2 mmol of CuI, 0.2 mmol of $In(Ac)_3$, 0.04 mmol of $SnCl_2$, 2 mL of OLA and 2 mL of ODE were loaded into a three neck flask and degassed for 20 min. The temperature was then elevated to 110 ^oC and N_2 gas was purged several times to ensure air and moisture-free environment inside the flask. The temperature was then further raised to 180 ^oC under N_2 environment and Se stock solution (0.3 mmol of Se dissolved in 0.3 mL of DPP and 0.5 mL of OLA) was injected swiftly. The flask was maintained at 180 ^oC for 10 min for the nucleation and growth of CISnSe core QDs. The temperature was then lowered to 90 ^oC and 10 mL of hexane was injected to rapidly cool down the CISnSe core QDs solution. The core QDs were purified using mixture of toluene and ethanol and stored in fridge for further characterization.

Synthesis of CISnSe/ZnSe core/shell QDs: 2 mL of original CISnSe core QDs solution was purified using toluene and ethanol for the growth of ZnSe shell. To grow ZnSe shell, 2 mL of the purified core QDs were dispersed in mixture of 3 mL of OLA/5 mL of ODE and degassed for 20 min. The mixture was then heated to 150 ^oC and 1.2 mL of zinc precursor solution (0.474 g of zinc stearate dissolved in 5 mL of ODE) was injected drop by drop and the temperature was maintained at 150 ^oC for 10 min. Afterwards, 1.2 mL of Se precursor solution (0.048 g of Se dissolved in 4 mL of TOP was injected slowly and the temperature was then elevated to 220 ^oC for 30 min to conduct shell growth. The reaction was then quenched by cooling down to room temperature. The CISnSe/ZnSe core/shell QDs were purified and stored in fridge for further characterization.

Fabrication of QDs-photodetector device: Patterned ITO substrates were washed with acetone and ethanol via ultrasonic machine for 30 minutes, followed by washing with deionized (DI) water for 30 minutes and dried with N_2 gas. A thick TiO_2 layer was grown on these substrates via tape casting, followed by drying at 120 °C for 6 minutes. Finally, the substrates were placed in the muffle furnace and sintered at 500 °C for 30 min. Later, the QDs were assembled in TiO_2 via electrophoretic deposition (EPD) technique (200V, 2 hours). As-prepared QDs-TiO_2 photoelectrode was treated with CTAB for ligand exchange and was further coated with 2 cycle-ZnS via successive ionic layer adsorption and reaction (SILAR) to protect the photo-oxidation. In a typical SILAR cycle process, the photoanode was successively immersed in 0.1 M solution of $Zn(Ac)_2$ for 1min and 0.1 M solution of Na_2S for 1min, which were rinsed by the corresponding solvents (methanol and methanol: DI-water) after each immersion cycle and dried by N_2 gas.

Characterization: TEM images, SAED patters, HAADF-STEM images and EDS elemental mapping of QDs were measured by using a FEI TECNAI G2 F20 TEM. XRD patterns were acquired by a Bruker D8 ADVANCE A25X with Cu Kα radiation. ICP-OES data were measured via an Agilent 5110 ICP-OES system. UV–visible absorption spectra were obtained by using a single monochromator UV-2600 spectrophotometer from SHIMADZU. PL spectrum and time-resolved PL decay curve of QDs were recorded by a HORIBA FluoroMax-4 fluorescence spectrometer using a 405 nm laser excitation source. PLQY of QDs was measured via a HORIBA Fluorolog-3 fluorescence spectrometer. ZEISS Gemini SEM 300 system equipped with an EDS detector was used to observe the cross-sectional SEM morphology and gain chemical composition mapping of QDs-based TiO_2 heterostructure. XPS data and UPS spectra (He I, 21.21 eV) were obtained by an ESCALAB 250Xi analyzer using monochromatic Al K_α radiation.

Device performance measurements: The photocurrent response, including *I-V* curves and *I-t* curves were measured by a Source Meter (Keithley 2450-EC) under different wavelength irradiation, as realized by using the lasers with wavelengths of 790 and 980 nm. The responsibility was calculated by:

$$R = \frac{I_l - I_d}{A \times P}(A/W)$$

(Equation S1)

Where I_l and I_d are the measured photocurrent and dark current, respectively. A is the area of active region. P is the power of the incident irradiation.

The calculation of detectivity was followed by:

$$D = \frac{R(A/W)}{\sqrt{2eJ_d}}(Jones)$$

(Equation S2)

Where R is calculated from Equation S1 and e is the elementary electron charge. J_d is the dark current density.

The calculation of external quantum efficiency (EQE) was followed by:

$$EQE = \frac{hcR}{q\lambda} \times 100\%$$

(Equation S3)

Where R is the responsivity and λ represents the specific wavelength of incident light.

Table S1. Lattice spacings measured from HRTEM images of QDs in **Figure 1**.

Lattice fringe	d_1	d_2
Length (nm)	0.332	0.329

Table S2. ICP-OES analysis for CISnSe/ZnSe core/shell QDs.

Elements	Cu	In	Se	Sn
Atomic concentration (%)	22%	31%	40%	7%

Table S3. The measured PLQY for CISnSe core and CISnSe/ZnSe core/shell QDs.

Sample name	CISnSe	CISnSe/ZnSe
QY (%)	0	2.3±0.2%

Table S4. Performance summary of CISnSe core and CISnSe/ZnSe core/shell QDs-based photodetectors.

Samples	**Wavelength (P)**	**Active area (cm^2)**	**Responsivity (A/W)**	**Detectivity (Jones)**
CISnSe	790 nm (0.5 mW)	0.035325	0	0
CISnSe	980 nm (0.5 mW)	0.035325	0	0
CISnSe/ZnSe	790 nm (0.5 mW)	0.035325	0.95	1.74×10^{10}
CISnSe/ZnSe	790 nm (1 mW)	0.035325	0.64	1.21×10^{10}
CISnSe/ZnSe	790 nm (2 mW)	0.035325	0.42	7.99×10^{9}
CISnSe/ZnSe	980 nm (0.5 mW)	0.035325	0.24	3.77×10^{9}
CISnSe/ZnSe	980 nm (1 mW)	0.035325	0.16	2.75×10^{9}
CISnSe/ZnSe	980 nm (2 mW)	0.035325	0.09	1.72×10^{9}
CISnSe/ZnSe	980 nm (5 mW)	0.035325	0.05	9.98×10^{8}

Table S5. Performance comparison for various eco-friendly QDs-based NIR photodetectors.

Device structure	Response range	R (AW^{-1})	$D^{\rightarrow}$ (Jones)	References
CISnSe/ZnSe QD/TiO_2	NIR (790 nm)	0.95	1.74 x 10^{10}	This work
MPA-$CuInSe_2$ /TiO_2	NIR (780 nm)	1.5 x 10^{-3}	2.1 x 10^{11}	[1]
Mn-CuInSe/TiO_2	NIR (780 nm)	3 x 10^{-2}	4.2 x 10^{12}	[2]
Au-$CuInSe_2$/SiO_2-Si	NIR (808 nm)	2.3 x 10^{-6}	-	[3]
Ag_2Se QDs/SiO_2-Si	MIR (2 μm)	0.03	-	[4]
Cu_2SnS_3 QDs/ITO	NIR (1064 nm)	1.89 x 10^{-3}	5.68 × 10^9	[5]
Ag_2Se QDs/TiO_2	NIR (1200 nm)	4.17 x 10^{-3}	-	[6]

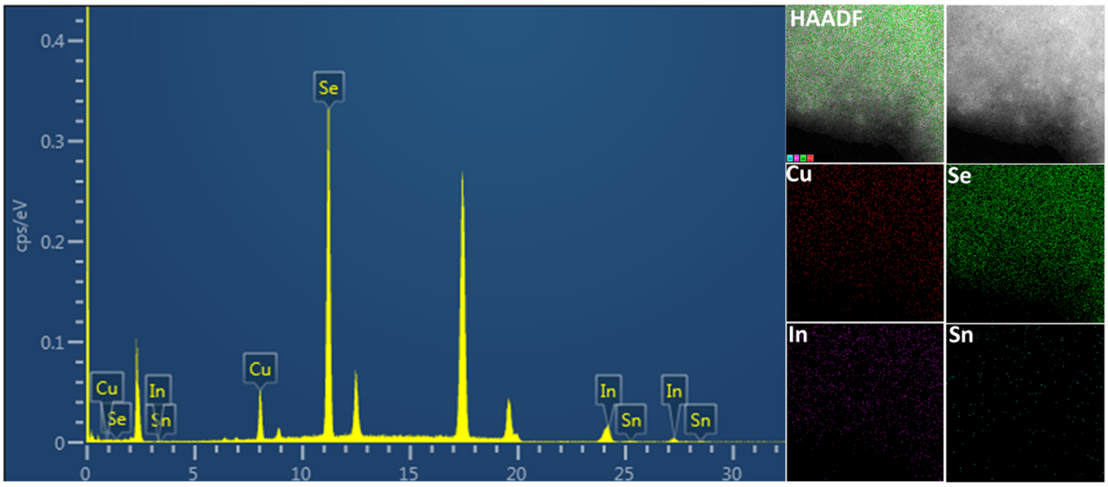

Figure S1. EDS spectrum, HAADF-STEM images and corresponding EDS elemental mapping of Cu, In, Sn and Se for CISnSe core QDs.

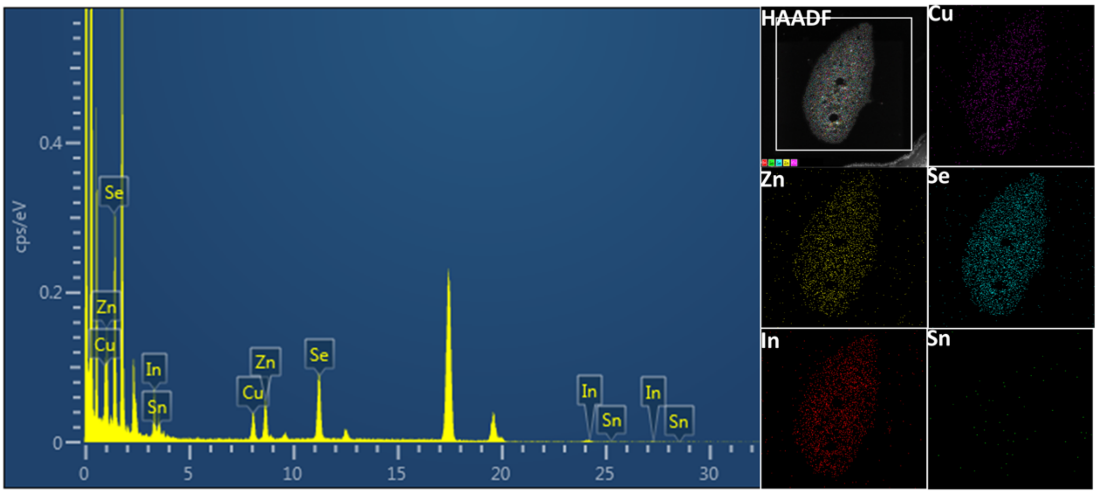

Figure S2. EDS spectrum, HAADF-STEM images and corresponding EDS elemental mapping of Cu, In, Sn, Zn and Se for CISnSe/ZnSe core/shell QDs

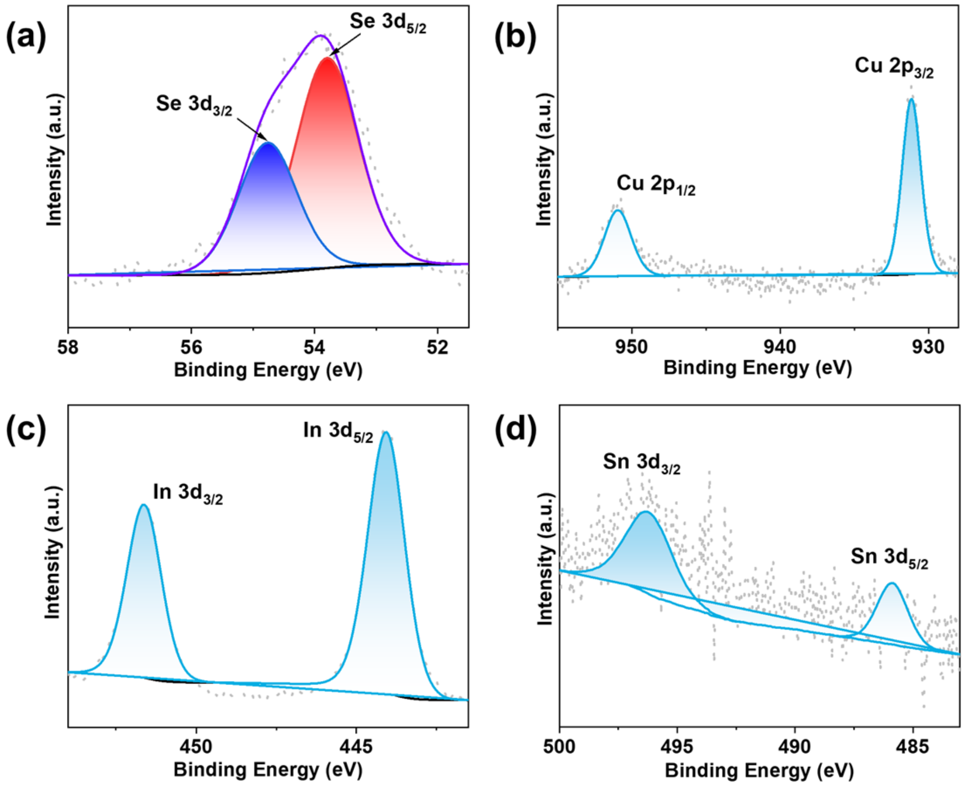

Figure S3. HR-XPS spectra of (a) Se 3d core levels for CISnSe core QDs. HR-XPS spectra of (b) Cu 2p, (c) In 3d and (d) Sn 3d core levels for CISnSe/ZnSe core/shell QDs.

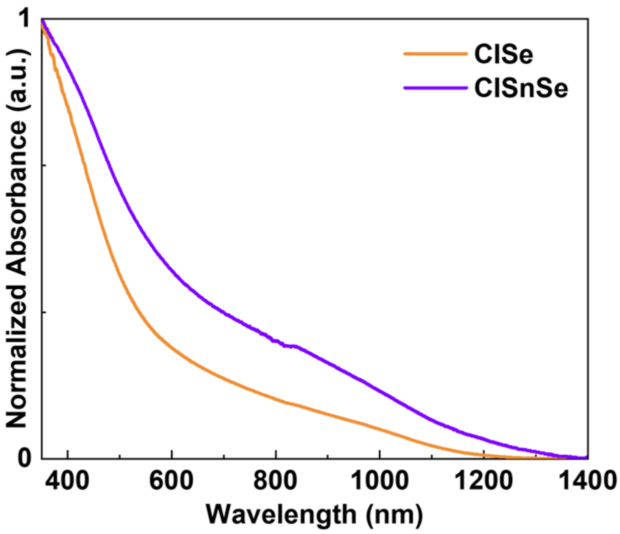

Figure S4. Comparison of absorption spectra for CISe and CISnSe core QDs.

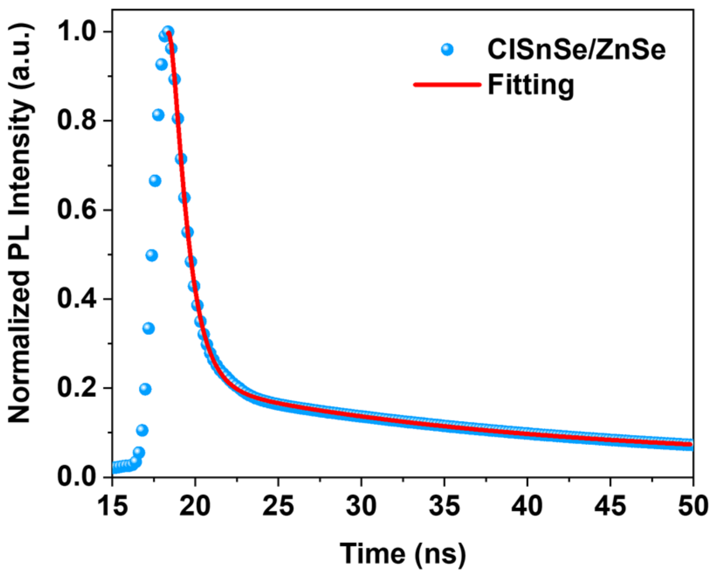

Figure S5. Time-resolved PL decay curve of CISnSe/ZnSe core/shell QDs with a fitted average lifetime of ~20 ns.

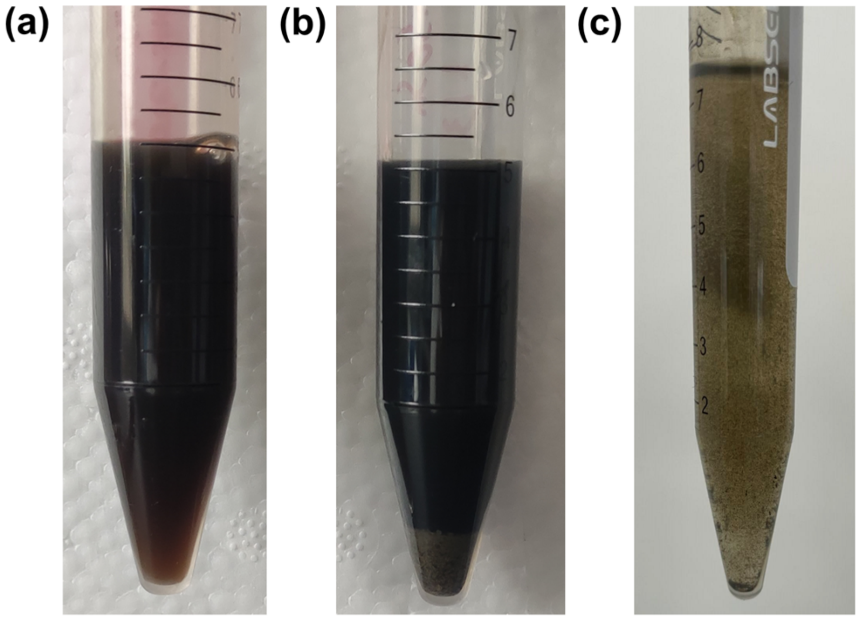

Figure S6. (a) CISnSe/ZnSe core/shell and CISnSe core stock QDs in toluene after 2-hour placement in air. (c) Corresponding diluted CISnSe core QDs from (b).

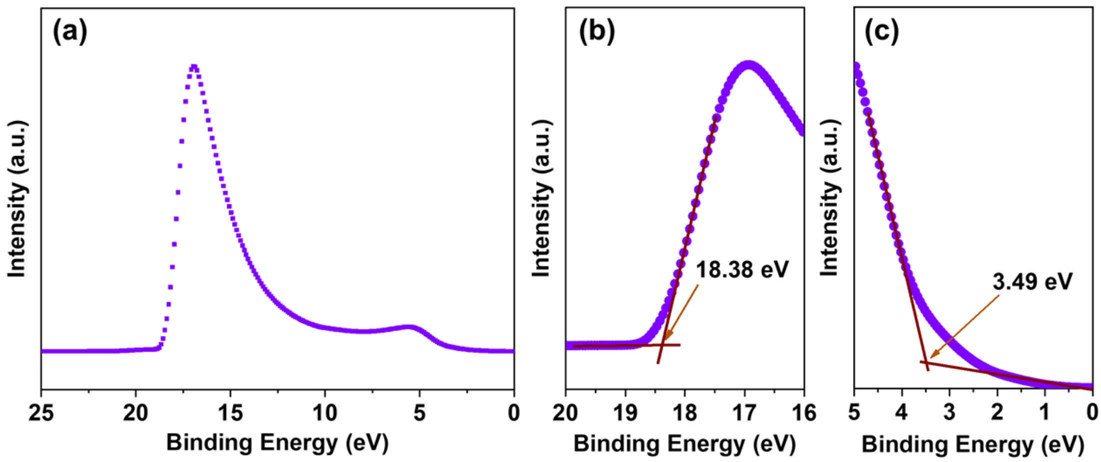

Figure S7. (a) UPS full spectrum and relevant (b) high energy cut-off and (c) low energy cut-off regions of CISnSe core QDs deposited on Si.

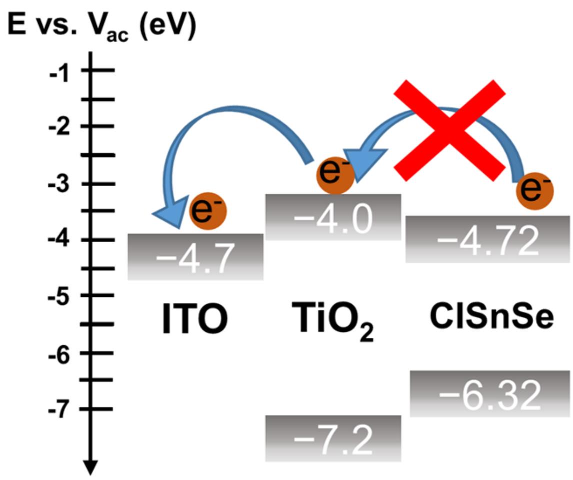

Figure S8. Approximate band alignment of CISnSe core QDs-TiO_2 heterostructure.

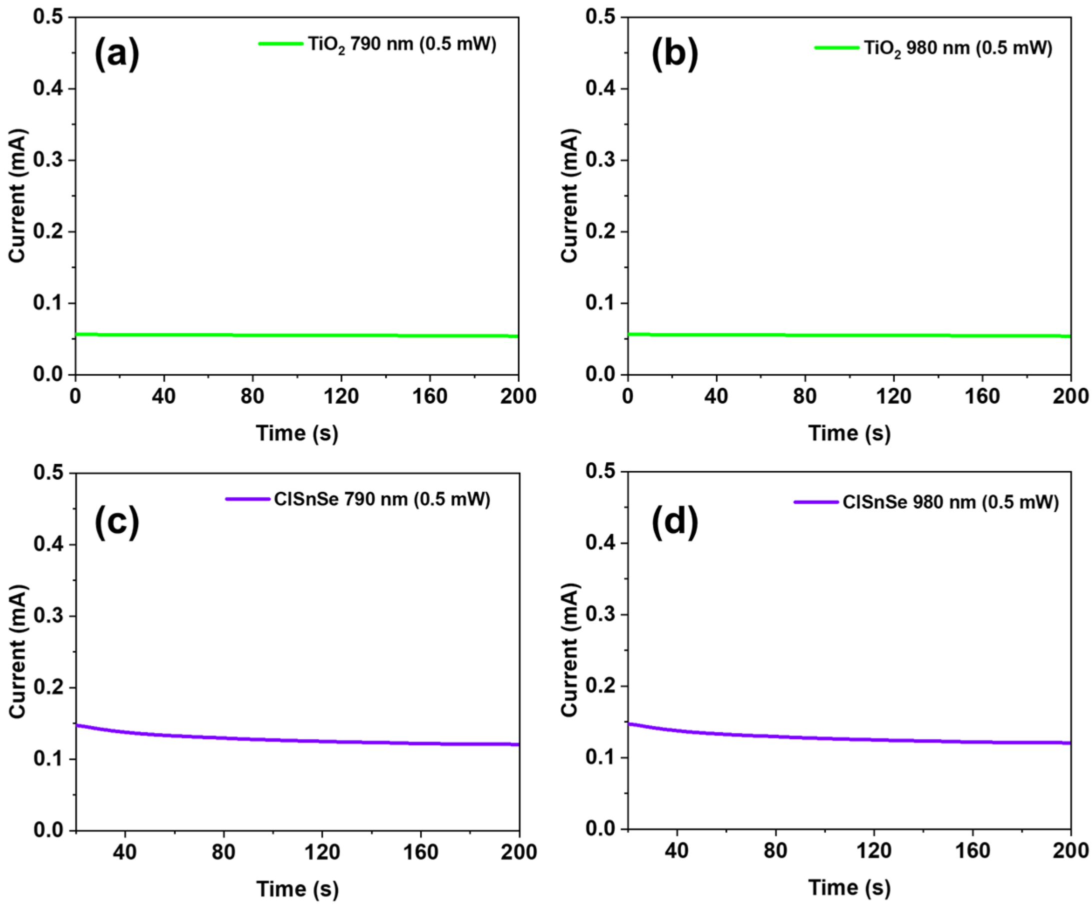

Figure S9. *I-t* curves of (a)-(b) bare TiO_2/ITO and (c)-(d) CISnSe core QDs/TiO_2/ITO photodetectors under 790 and 980 nm NIR illumination (0.5 mW).

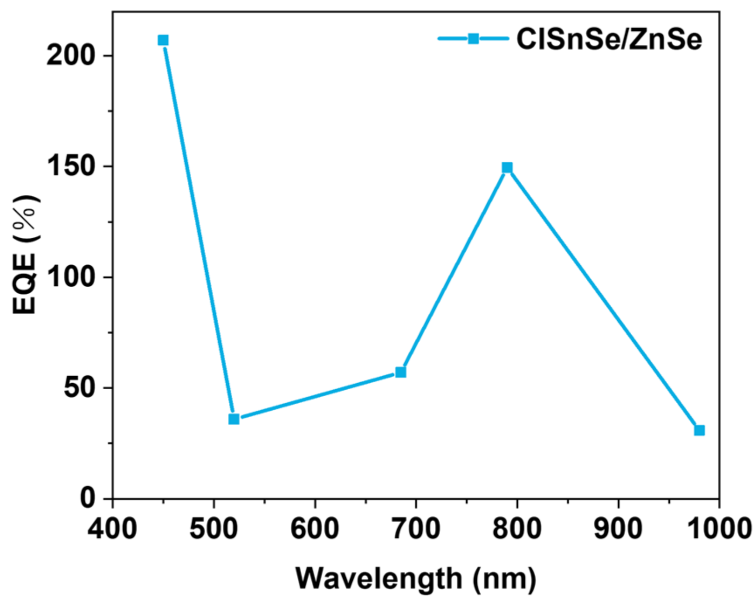

Figure S10. EQE spectrum of CISnSe/ZnSe core/shell QDs-based photodetectors measured under 450, 520, 685, 790 and 980 nm (0.5 mW).

References

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