Electronic supplementary information

Halide Removal and SiO_2@TiO_2 Composite Passivation: Enhancing InP QD Photooxidation Stability for WLEDs

Yuyuan Fu[†, a], Yujie Song[†, a], Qixin Weng[a], Wenda Zhang*[, a], Changsheng Cao*[, b], Yujie Song*[, a]

[a]*School of Chemistry and Chemical Engineering, Hainan University, Haikou 570228, China*

[b]*Key Laboratory of Advanced Carbon-Based Functional Materials (Fujian Province University), Fuzhou University, Fuzhou 350016, Fujian, China*

†*These authors contributed equally.*

* Corresponding authors.

E-mail addresses:

songyujie@hainanu.edu.cn (Y. Song);

cscao@fzu.edu.cn (C. Cao);

zhangwenda@hainanu.edu.cn (W. Zhang)

Physical characterization

UV-Vis Absorption Spectroscopy. The UV-Vis absorption spectra were measured using a Shimadzu UV-2600 spectrophotometer.

Emission Spectroscopy. The emission spectra were determined with a Tianjin Gangdong F-320 fluorescence spectrophotometer equipped with a 150 W xenon lamp.

X-ray Diffraction (XRD). XRD measurements were carried out using a Rigaku high-power variable-temperature X-ray diffractometer. The sample preparation procedure was as follows: A solution of QDs dissolved in hexane was dropped onto a dry silicon substrate. After allowing the hexane to completely evaporate by standing, the sample was ready for testing.

X-ray Photoelectron Spectroscopy (XPS). XPS measurements were performed using a Shimadzu KRATOS Axis Supra X-ray photoelectron spectrometer: A solution of QDs dissolved in hexane was dropped onto a dry silicon substrate and left to stand until the hexane had completely evaporated before testing.

Transmission Electron Microscope (TEM). TEM and EDS analyses were performed using a Thermo Scientific Talos F200X G2 microscope: The purified sample obtained from centrifugation was dispersed in hexane and drop-cast onto a copper grid for measurement.

Photoluminescence Quantum Yield (PLQY). PLQY was measured using the steady-state and transient fluorescence spectrometer (FLS1000, Edinburgh Instruments, UK). For the measurement, the etched InP QDs (without further centrifugation) were dispersed in hexane within a quartz cuvette, with the absorbance at the excitation wavelength (365 nm) precisely adjusted to 0.1. PLQY was then determined using the integrating sphere system.

Stability Testing. The stability of quantum dots (QDs) was tested by exposing them to UV light irradiation (wavelength: 365 nm) under the conditions of 60°C and 90% relative humidity.

Experimental

Materials

Indium(III) chloride ($InCl_3$, 99.99 %), zinc(II) chloride ($ZnCl_2$, 99.99 %), indium(III)

iodide (InI_3, 99.99 %), zinc acetate ($Zn(OAc)_2$, 99.99%), zinc(II) bromide ($ZnBr_2$, 99.99 %), indium(III) acetate ($In(OAc)_3$, 99.99 %), oleylamine (OLA, 90 %), palmitic acid, (90%), tris(dimethylamino)phosphine ($(DMA)_3P$, 97 %), tris(trimethylsilyl)phosphine ($(TMS)_3P$, 10 wt % in hexane), zinc acetate, palmitic acid, zinc stearate ($Zn(St)_2$, 10-12% Zn), 1-octadecene (ODE, >90 %), tri-n-octylphosphine (TOP, 97 %), 1-dodecanethiol (DDT, 98 %), sulfur powder (S, 99.98 %), selenium powder (Se, 99.99 %), tetramethyl orthosilicate (TMOS, 98 %), tetrabutyl titanate (TBT, 98 %), toluene (TOL, 99 %), n-hexane, and ethanol were purchased from Sigma-Aldrich and used without further purification.

Stock Solutions

$Zn(St)_2$-ODE: $Zn(St)_2$ (2.5 g) was dissolved in 10 mL of degassed ODE under magnetic stirring to afford a clear solution.

TOP-Se (1.9 M): Se powder (15.2 mmol) and TOP (8 mL) were heated to 100 °C in a 20 mL vial with stirring until a colorless, homogeneous solution formed.

TOP-S (2.2 M): S powder (17.5 mmol) and TOP (8 mL) were heated to 100 °C in a 20 mL vial with stirring until complete dissolution.

Synthesis of red-emitting InP/ZnSe/ZnS QDs (InP/ZnSe/ZnS QDs-with-Cl)

$InCl_3$ (0.452 mmol) and $ZnCl_2$ (2.2 mmol) were charged into a 50 mL three-neck flask with OLA (9 mL). The mixture was degassed at 120 °C for 1 h under vacuum to remove trace water and oxygen. Under nitrogen, the solution was heated to 190 °C, and $(DMA)_3P$ (2.42 mmol, 0.50 mL) was rapidly injected. The reaction was held at 190 °C for 21 min to grow InP cores. The temperature was then raised to 200 °C, and $Zn(St)_2$-ODE solution (6 mL) together with TOP-Se (1.9 M, 0.8 mL) was added slowly. Subsequently, the temperature was increased to 300 °C; TOP-S (2.2 M, 0.4 mL) was injected and reacted for 5 min, followed by rapid addition of dodecanethiol (1.5 mL) and a final growth step at 300 °C for 40 min to complete the ZnS shell. The reaction mixture was cooled to room temperature prior to further processing.

Synthesis of green-emitting InP/ZnSe/ZnS QDs

InI_3 (0.38 mmol, 0.168 g) and $ZnBr_2$ (2.2 mmol, 0.495 g) were loaded into a 50 mL three-neck flask together with OLA (5 mL). The mixture was degassed at 120 °C for 1 h to remove residual water and oxygen. Under a nitrogen atmosphere, the solution was heated to 200 °C, at which point $(DMA)_3P$ (2.3 mmol, 0.45 mL) was swiftly injected. The reaction was maintained at 200 °C for 21 min to nucleate InP cores. The temperature was then raised to 280 °C, and $Zn(St)_2$ solution (6 mL) together with TOP-Se (1.9 M, 0.6 mL) was added dropwise over 5 min; after 20 min at 280 °C, TOP-S (2.2 M, 0.4 mL) was introduced and the mixture was held at 300 °C for 20 min. Finally, dodecanethiol (1.5 mL) was rapidly injected and the reaction was kept at 300 °C for 40 min to complete the ZnS outer shell. The reaction mixture was allowed to cool to room temperature before work-up. The PLQY of the green-emitting InP/ZnSe/ZnS QDs was measured to be 82%.

Synthesis of halide-free InP/ZnSe/ZnS QDs (InP/ZnSe/ZnS QDs-free-Cl)

$In(OAc)_3$ (0.15 mmol) and $Zn(OAc)_2$ (0.075 mmol) were loaded into a 50 mL three-neck flask together with OLA (5 mL). The mixture was degassed at 120 °C for 1 h under vacuum to remove residual water and oxygen. Under nitrogen, the solution was heated to 270 °C, at which point $(DMA)_3P$ (2.3 mmol, 0.45 mL) was swiftly injected. The reaction was maintained at 270 °C for 21 min to nucleate InP cores. The temperature was then raised to 280 °C, and $Zn(St)_2$ solution (6 mL) together with TOP-Se (1.9 M, 0.6 mL) was added dropwise, after 20 min at 280 °C, TOP-S (2.2 M, 0.4 mL) was introduced and the mixture was held at 300 °C for 20 min. Finally, dodecanethiol (1.5 mL) was rapidly injected and the reaction was kept at 300 °C for 40 min to complete the ZnS outer shell. The reaction mixture was allowed to cool to room temperature before work-up.

Purification of InP/ZnSe/ZnS QDs

Crude InP/ZnSe/ZnS QDs were dispersed in n-hexane and centrifuged at 10,000 rpm for 2 min; the precipitate was discarded. The supernatant was mixed with ethanol to

induce flocculation, followed by centrifugation at 10,000 rpm for 2 min. The supernatant was removed and the cycle repeated three times to give purified QDs.

Halide-removal treatment

The purified QDs were re-dispersed in a mixture of 70 mL OLA and 5 mL DDT in a 100 mL three-neck flask. The mixture was degassed at 120 °C for 1 h, then heated to 300 °C under N_2 and maintained for 30 min to desorb surface-bound halide ions.

Synthesis of InP@SiO_2 QDs

The purified QDs were dissolved in toluene (0.5 mg mL^{-1}). TMOS (100 μL) was added to 20 mL of this QD-toluene solution. The mixture was stirred at 100 rpm, 25 °C, 60-70 % RH for 6 h to complete hydrolysis/condensation.

Synthesis of InP@SiO_2@TiO_2 QDs

An identical QD-toluene solution (0.5 mg mL^{-1}, 20 mL) was treated with TMOS (100 μL) under the same conditions for 3 h. TBT (100 μL) was then injected and stirring continued at 100 rpm, 25 °C, 60-70 % RH for 4 h to deposit the TiO_2 over-layer.

WLED fabrication

Red and green InP@SiO_2@TiO_2 QDs were dispersed in optical-grade silicone at a weight ratio of 1:10. The blend was drop-cast onto a 446 nm blue LED chip and cured under 365 nm UV irradiation for 1 min to yield the final white-light-emitting device.

Table S1 PLQY and fluorescence lifetimes of the QDs samples in solution and film states.

	PLQY	fluorescence lifetime (ns)
QDs-free-Cl (solution)	75%	58.08
QDs-with-Cl (solution)	70%	55.30
QDs-Cl-desorbed (solution)	67%	52.92
QDs (film)	30%	30.22
QDs@SiO_2 (film)	25%	24.88
QDs@SiO_2@TiO_2 (film)	24%	22.55

Table S2 The surface Cl^- content of QDs-Cl-desorbed and QDs-with-Cl

Precursor	Cl
InP/ZnSe/ZnS QDs-Cl-desorbed	4.45%
InP/ZnSe/ZnS QDs-with-Cl	16.13%

Table S3 PLQY of the QDs samples across solvents with different polarities

	n-hexane	toluene	chloroform
QDs-free-Cl	75%	73%	70%
QDs-Cl-desorbed	67%	65%	61%
QDs-with-Cl	70%	68%	66%

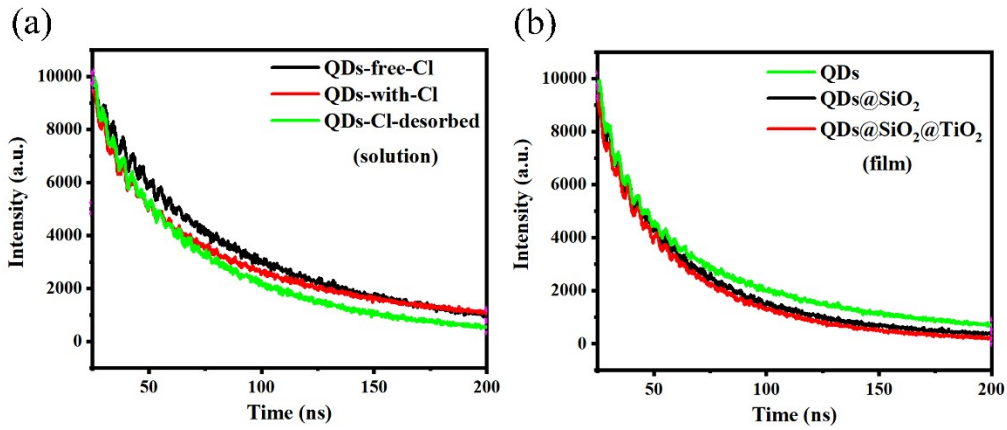

Fig. S1 Comparison of fluorescence lifetimes of (a) QDs solutions (QDs-free-Cl, QDs-Cl-desorbed, and QDs-with-Cl) and (b) QDs films (QDs, QDs@SiO_2, and QDs@SiO_2@TiO_2).

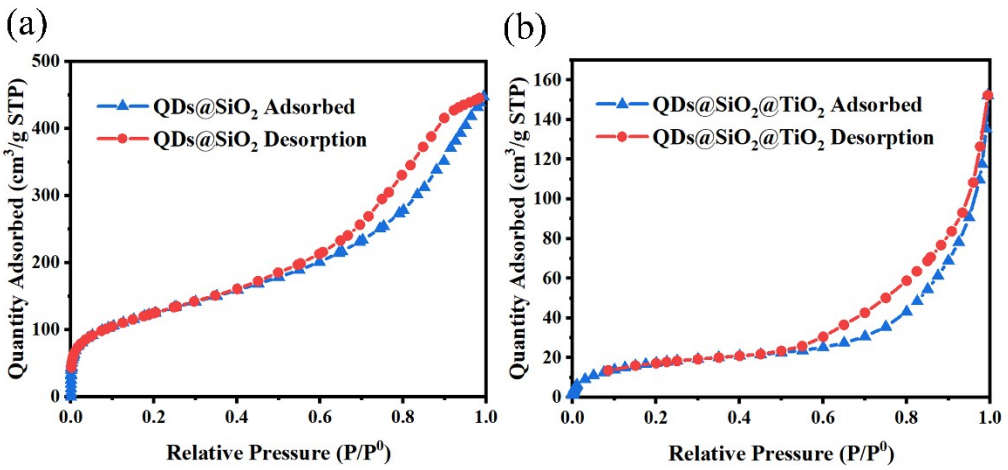

Fig. S2 BET adsorption curves of (a) QDs@SiO_2 and (b) QDs@SiO_2@TiO_2.

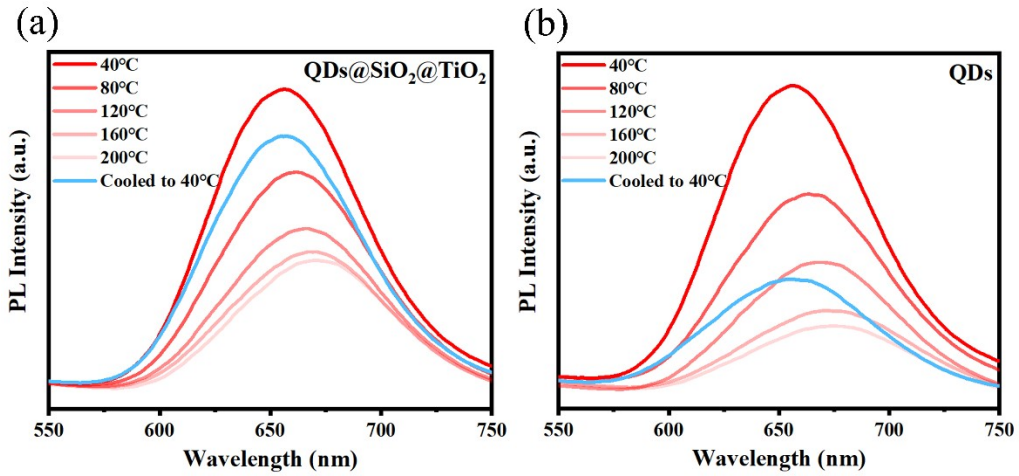

Fig. S3 Temperature-dependent photoluminescence spectra of (a) QDs@SiO_2@TiO_2 and (b) QDs.

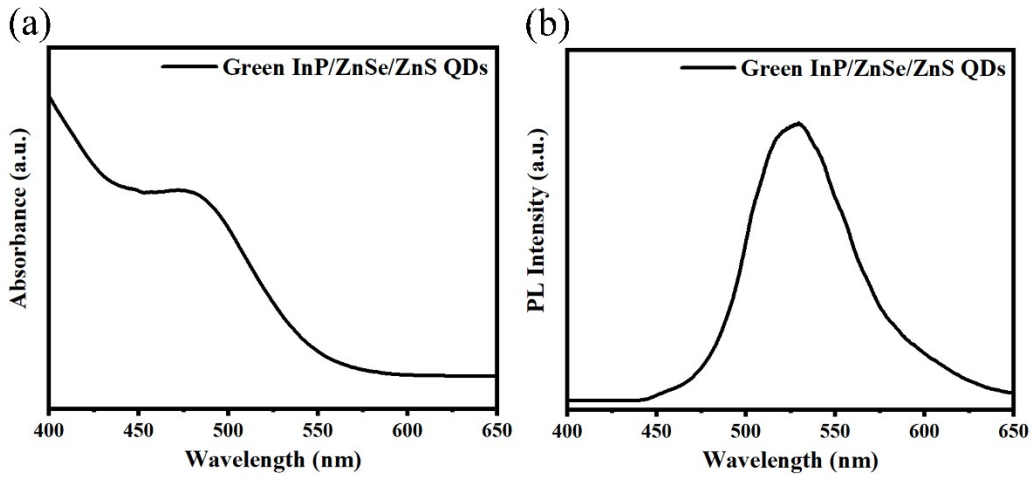

Fig. S4 (a) UV-vis absorption spectrum and (b) PL spectrum of Green InP/ZnSe/ZnS QDs.