

Supporting Information

Interface Defects Repair of Core/Shell Quantum Dots through Halide Ions Penetration

Changwei Yuan,^a Mengda He,^a Xinrong Liao,^a Mingming Liu,^a Qinggang Zhang,^a Qun Wan,^b
Zan Qu,^a Long Kong,^{*a} Liang Li^{*b}

^aSchool of Environmental Science and Engineering, Shanghai Jiao Tong University

Shanghai 200240, P. R. China.

*^bMacao Institute of Materials Science and Engineering (MIMSE), Macau University of Science
and Technology, Taipa, Macao 999078, P. R. China.*

**E-mail: lli@must.edu.mo, longmao88@sjtu.edu.cn*

Methods

Chemicals. Indium acetate ($\text{In}(\text{OAc})_3$, 99.99%), selenium powder (Se, 99.999%), sulfur (S, 99.99%), palmitic acid (PA, 99%), zinc acetate ($\text{Zn}(\text{OAc})_2$, 99.99%), zinc chloride (ZnCl_2 , 99.999%), zinc bromide (ZnBr_2 , 99.999%), zinc iodide (ZnI_2 , 99.999%), Cadmium Oxide (CdO , 99.99%), benzoyl peroxide (BPO, 75%), 1-octadecene (ODE, 90%), oleylamine (OAM, 70%), oleic acid (OA, 90%), and trioctylphosphine (TOP, 97%) were purchased from Sigma-Aldrich. Toluene (HPLC, 99.5%), hexane (HPLC, 99.5%), acetone (HPLC, 99.5%) were purchased from Sinopharm Reagents. Methyl alcohol (HPLC, 99.9%) was purchased from Fisher. 1-octadecene was evacuated at 150 °C for 2 h prior to use. All other chemicals were stored in glove box without further purification.

Preparation of precursor. 0.3 M $\text{Zn}(\text{OA})_2$ precursor was prepared with 24 ml of OA and 36 mmol of $\text{Zn}(\text{OAc})_2$ in 96 ml ODE, and the mixture was evacuated at 120 °C for 2 h and heated to 280 °C for 10 min with argon bubbling. For 1 M TOP-S and 2 M TOP-Se precursors, 20 mmol S powder and 40 mmol Se powder were dissolved in 20 ml of TOP, respectively. 0.01 M BPO was prepared by ultrasonic dissolving 0.1 mmol BPO in 10 ml toluene.

Synthesis of In(Zn)P/ZnSe. $\text{In}(\text{OAc})_3$ (0.4 mmol), $\text{Zn}(\text{OAc})_2$ (0.3 mmol), and PA (1.8 mmol) were mixed with 12 ml ODE in a 50 ml flask, the flask was evacuated at 120 °C for 2 h and bubbled with argon at 150 °C for 1 h. During this step, the solution changed clear. Afterward, the solution was heated to 300 °C under argon, then a mixture containing 0.2 mmol $(\text{TMS})_3\text{P}$ and 1ml TOP was quickly injected into the solution at 300 °C. The reaction temperature was decreased to 280 °C for 5 min for the growth of InP QDs. Into the flask, the TOP-Se (1 M, 0.4 ml) was injected. After 5 min, the $\text{Zn}(\text{OA})_2$ stock solution (0.3 M, 2 mL) was added into the reaction

flask and reacted for 20 min to form InP/ZnSe QDs. The reaction was stopped by cooling down to room temperature. The purification schemes of InP/ZnSe QDs refer to the reported article.

Synthesis of the In(Zn)P/ZnSe/ZnSeS/ZnS QDs. For further shell growth of ZnSeS and ZnS, the purified InP/ZnSe QDs, Zn(OA)₂ (0.3 M, 12 ml) and 10 ml ODE were added into a 100 ml flask. After evacuating at 80 °C for 1 h, the flask was purged with argon and then the temperature was increased to 300 °C. A mixture of TOP-Se (2 M, 1ml) and TOP-S (1 M, 1 ml) were injected into the reaction mixture and maintained for 1 h to grow the ZnSeS shell. Afterword, TOP-S (1 M, 3 ml) and Zn(OA)₂ (0.3 M, 10 ml) were injected into the reaction mixture, and then heated up to 310 °C for 1 h to grow the ZnS shell.

Synthesis of CdSe/ZnS and InP/ZnSeS core-shell QDs with BPO treated. For the synthesis of CdSe/ZnS, 1.2 mmol CdO, 4.8 mmol OA and 15 ml ODE were introduced in a 50 ml flask. The flask was evacuated at 80 °C for 1 hour, after the flask was bubbled with argon and the temperature was increased to 240 °C maintained for 1 h. Subsequently, the reaction temperature was raised to 270 °C, a mixture of 0.4 mmol Se powder and 2 ml ODE was quickly injected into the reaction solution, which decreased the temperature to 230 °C. The flask was maintained at that temperature for 30 s and rapidly cooled down to room temperature in an ice-water bath to prepare CdSe core. The CdSe core was purified five times with methanol and hexane at 50 °C, and re-dispersed in toluene as stock solution, showed an optical density of 2 at first exciton absorption peak. Before the shell growth, the CdSe QDs were treated with surface oxidation by BPO. The treatment process was to add 100 µl BPO (0.01 M) to 4 ml CdSe stock solution, and to stir in an oil bath at 50 °C for 1 h. Then the oxidized CdSe solution was purified one times with acetone and toluene. For further growth of ZnS, the purified oxidized CdSe QDs, Zn(OA)₂ (0.3 M, 12 ml) and 10 ml ODE were added into a 100 ml flask. After evacuating at 80 °C for 1 hour,

the flask was purged with argon and then the temperature was increased to 280 °C. Then TOP-S (1 M, 3 ml) was injected at 1.5 ml h⁻¹ and maintained for another 1 h to grow the ZnS shell. To prepare the BPO treated InP/ZnSeS, the shell growth scheme was the same as above, except that the InP cores were purified before shell growth and treated with BPO at 50°C for 1 h.

Post-treatment of QDs with Zinc halides or OAM halides. 0.2 M zinc halides were prepared by dissolving 2 mmol ZnCl₂, ZnBr₂, and ZnI₂ in the 10 ml mixed solvent (V_{OAM}:V_{ODE}=2:13) of OAM and ODE, respectively. 0.1 M OAM halides were prepared by dissolving 1 mmol OAM-Cl, OAM-Br, and OAM-I in the 10 ml ODE, respectively. The post-treatment of QDs was conducted as follows: 6 ml crude solution of core-shell QDs was added to 50 ml flask, then the solution was purged with argon and the temperature was increased to 300 °C (the temperature for CdSe/ZnS is 240 °C). 2 ml Zinc halides or OAM halides were injected at 4 ml h⁻¹ and maintained the temperature for another 30 min. The synthesized QDs were purified by five times with methanol and hexane at 50 °C and then purified two times with acetone and toluene, finally the QDs were dispersed in toluene for further characterization.

Etching QDs. The purified QDs were diluted in toluene, showing an optical density of 1 at first exciton absorption peak. Diluted HCl in acetone (1 M, 50 μl) was drop by drop into the cuvette containing QDs solution (2 ml), and the QDs were etched for 10 min. Then, the remaining QDs were washed three times with acetone and centrifuged at 10000 rpm. The colorless supernatant was taken out for ICP-OES and ion chromatography tests. And the precipitates were dispersed in toluene, performing subsequent etching. This process will be repeated many times until the QDs were completely etched.

Characterization. Photoluminescence spectra and absorption spectra were measured with a fluorescence spectrometer (F-380, Tianjin Gangdong Sci.&Tech.) and an UV-vis

spectrophotometer (Cary-60, Agilent), respectively. The photoluminescence quantum yield was performed with a spectrophotometer (FLS1000, Edinburgh) with a pre-calibrated integrating sphere (N-M01). The QDs were diluted in toluene and measured in a standard quartz cuvette (10 mm×10 mm), which were excited at 365 nm. Time-resolved photoluminescence decay spectra were also collected with Edinburgh spectrophotometer by a 365 nm pulsed diode laser excitation source. The powder X-ray diffraction patterns were measured with a Bruker X-ray Diffractometer (XRD-6100, Shimadzu). The morphologies of QDs were observed by field emission transmission electron microscope (TALOS F200X, Thermofisher) instruments. The surface element compositions and chemical states of samples were analyzed by an X-ray photoelectron spectrometer (AXIS UltraDLD, Shimadzu). Solid-state ³¹P NMR experiments were recorded on a 600 MHz nuclear magnetic resonance spectrometer (AVANCE NEO, Bruker). ³¹P high-power decoupling spectra were performed with a recycle delay of 30 s. Quantitative analysis of cations was by an inductively coupled plasma optical emission spectrometer (ICP-OES 5100, Agilent). And the quantitative analysis of anions was by an ion chromatograph (ICS-5000+/900, Thermofisher).

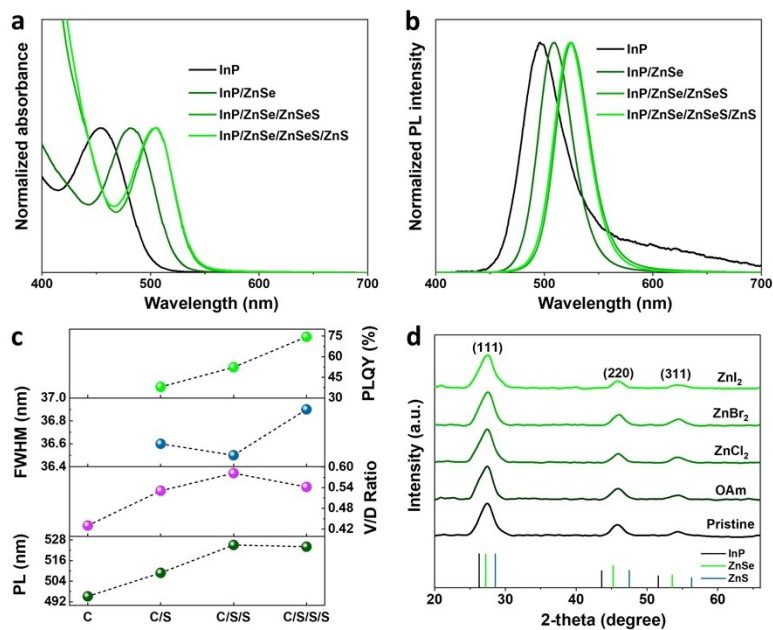


Figure S1. (a) Optical absorption, (b) normalized PL spectra and (c) optical properties numerical plot of InP cores, core-multishell QDs. (d) XRD patterns of pristine (black line) and post-treated (green lines) InP core-multishell QDs.

Table 1. Lifetime components of pristine and post-treatment QDs.

Sample	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_{avg} (ns)	PLQY
Pristine	25.4	50.1	69.6	49.9	47.4	73.5
OAm	25.9	61.0	62.6	39.0	40.2	70.5
ZnCl₂	28.2	75.3	65.9	24.7	37.5	84.1
ZnBr₂	28.9	79.2	68.4	20.8	37.1	86.0
ZnI₂	26.8	66.2	60.9	33.8	38.3	79.7

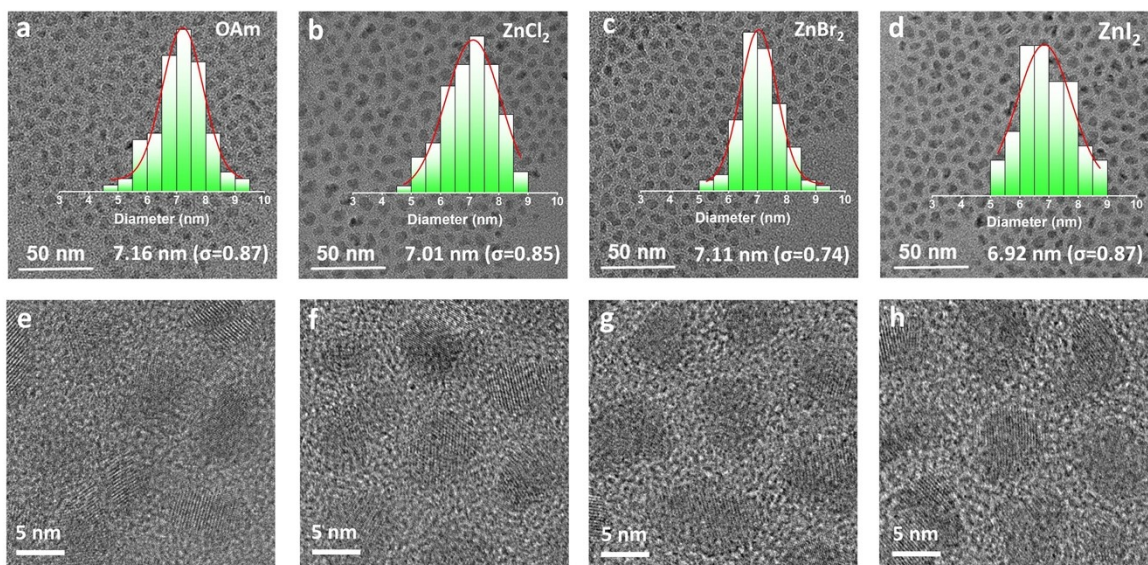


Figure S2. (a-d) Lower-resolution and (e-h) higher-resolution TEM images of InP core-multishell QDs post-treated with OAm, $ZnCl_2$, $ZnBr_2$, and ZnI_2 , respectively. The insets in a–d show the corresponding size distribution histograms.

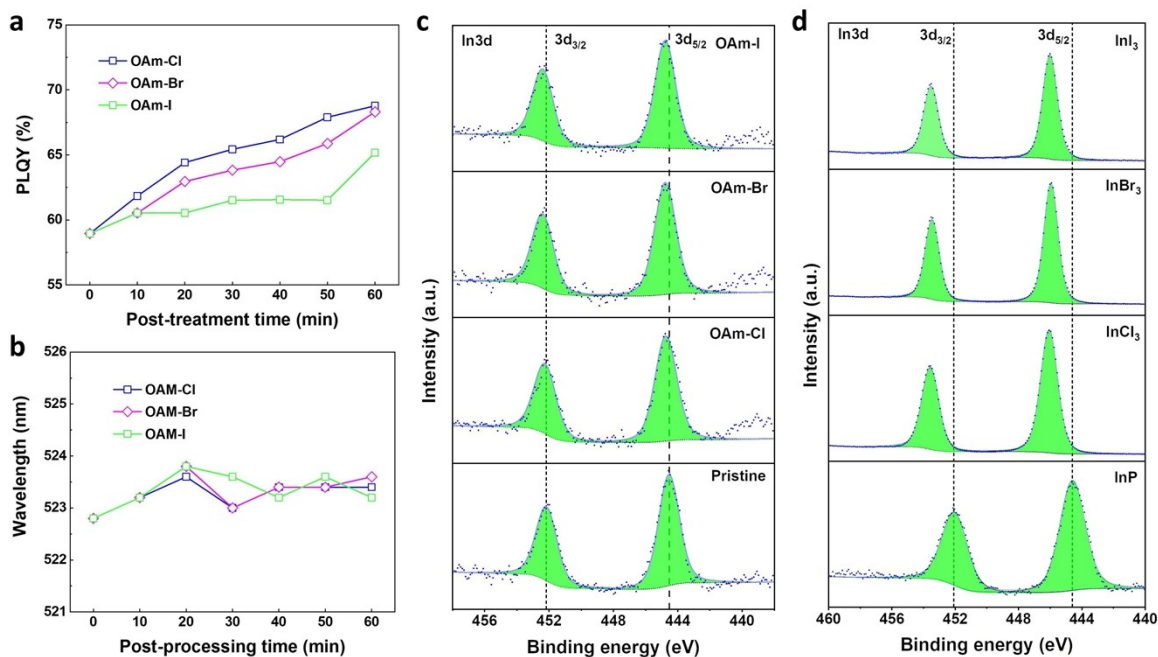


Figure S3. Variation of (a) PLQY and (b) PL peak positions of InP core-multishell as a function of OAm halides post-treatment time. High-resolution In 3d XPS spectra of (c) pristine InP/ZnSe/ZnSeS/ZnS QDs, InP/ZnSe/ZnSeS/ZnS QDs post-treated with OAm-Cl, OAm-Br, and OAm-I, (d) pristine InP/ZnSe/ZnSeS/ZnS QDs, InCl₃, InBr₃, and InI₃.

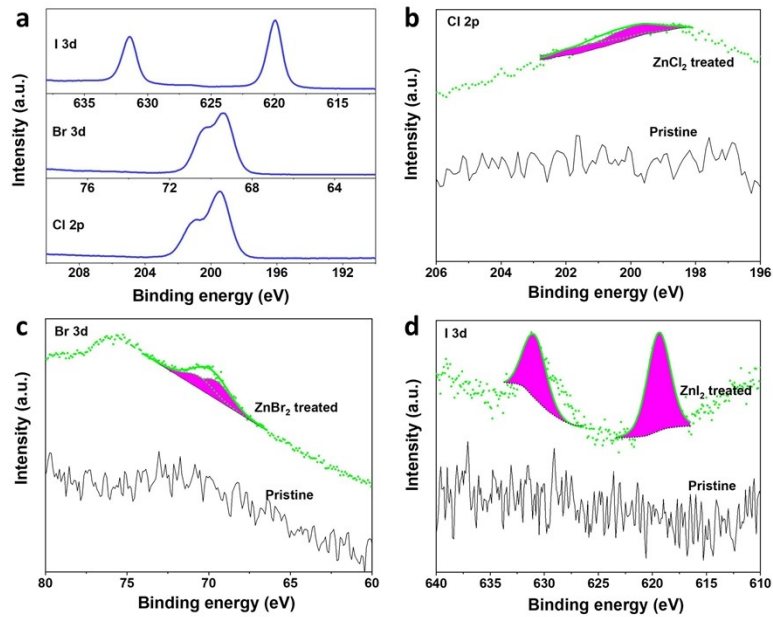


Figure S4. (a) Cl 2p, Br 3d, and I 3d XPS spectra of InCl₃, InBr₃, and InI₃. (b) Cl 2p, (c) Br 3d, and (d) I 3d XPS spectra of InP core-multishell QDs post-treated with ZnCl₂, ZnBr₂, and ZnI₂.

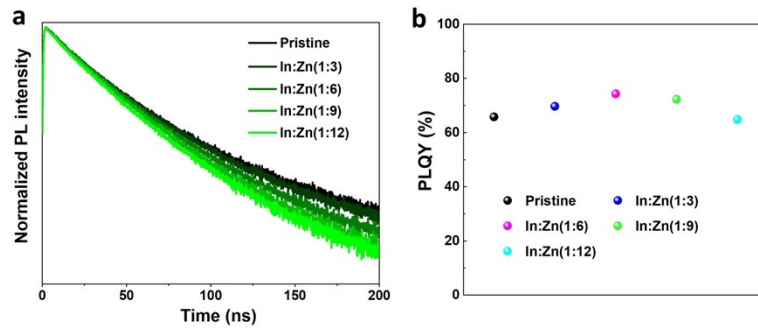


Figure S5. (a) Normalized PL spectra and (b) PLQY of post-treated InP core-multishell QDs with different ZnBr_2 amounts, the ratios of $\text{InPA}_3:\text{ZnBr}_2$ vary from 1:0 to 1:12.

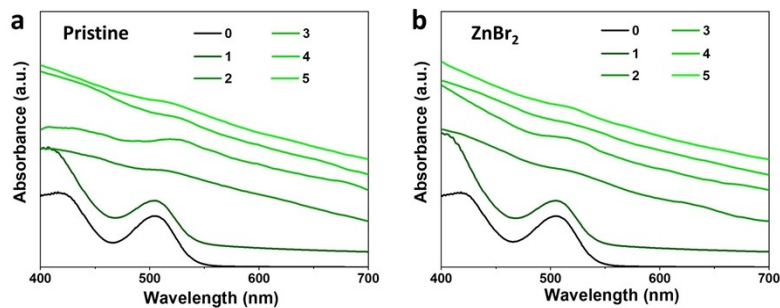


Figure S6. Optical absorption spectra of (a) pristine and (b) ZnBr₂ treated InP core-multishell QDs with different etching times.

It is observed that the absorption spectra of pristine and ZnBr₂ treated samples red shift with the increase of etching times, which would be attributed to the agglomeration of QDs caused by the removal of long-chain ligands.

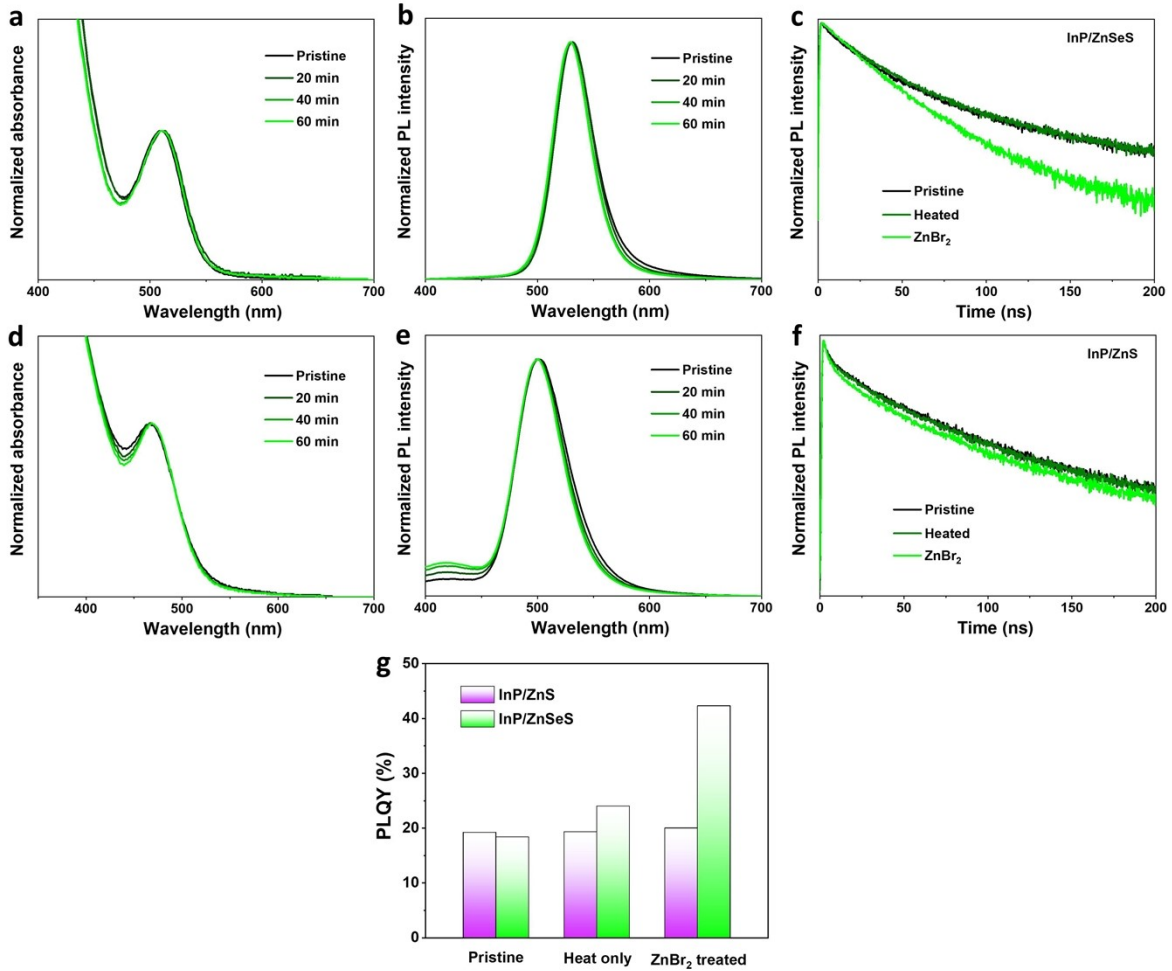


Figure S7. Measured absorbance and normalized PL intensity spectra of (c) InP/ZnSeS and (d) InP/ZnS QDs with different ZnBr₂ post-treated times. PL decay spectra of (c) InP/ZnSeS and (d) InP/ZnS, which were prepared without any post-treatment, with heat only and ZnBr₂ post-treatment, respectively. (g) PLQY values of core-shell QDs corresponding to the above different post-treatment conditions.

The InP/ZnSeS QDs were prepared with an oxidized core to demonstrate the role of halides post-treatment in reducing oxidation defects within the shells. While the InP/ZnS QDs were coated with a thick ZnS shell, leading to substantial interfacial stress due to the lattice mismatch between the ZnS shell and the InP core. It is observed that the PLQY of InP/ZnSeS QDs with

oxidation defects could be significantly improved, proving the traps inside the shell could be passivated by ZnBr_2 post-treatment. In addition, the PLQY of thick shell InP/ZnS almost unchanged before and after ZnBr_2 treatment, suggesting that the impact of ZnBr_2 post-treatment on relieving interfacial stress was limited.

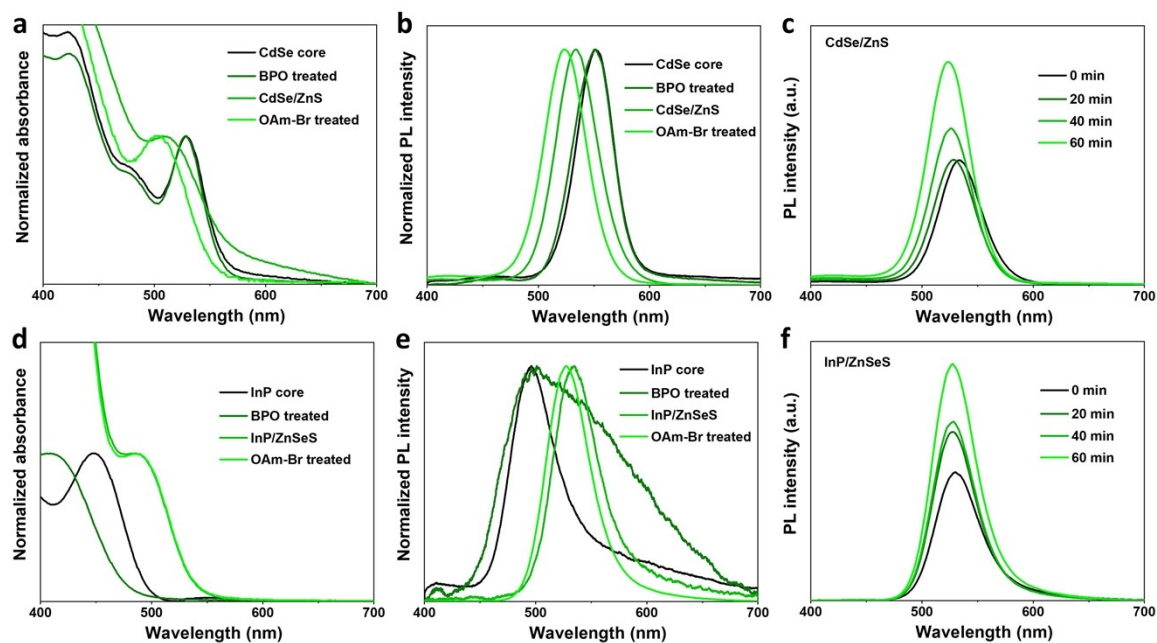


Figure S8. Measured optical absorbance and normalized PL intensity spectra of the following QDs: (a, b) CdSe core, CdSe core with BPO treated, CdSe/ZnS, CdSe/ZnS with OAm-Br treated, and (d, e) InP core, InP core with BPO treated, InP/ZnSeS, InP/ZnSeS with OAm-Br treated. The PL intensity spectra of OAm-Br treated (c) CdSe/ZnS and (f) InP/ZnSeS QDs changed with post-treatment time. Both the CdSe/ZnS and InP/ZnSeS QDs with oxidized cores.