Supporting Information

Ga for Zn Cation Exchange Allows for Highly Luminescent and Photostable InZnP based Quantum Dots

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Growth of larger InZnP core QDs.

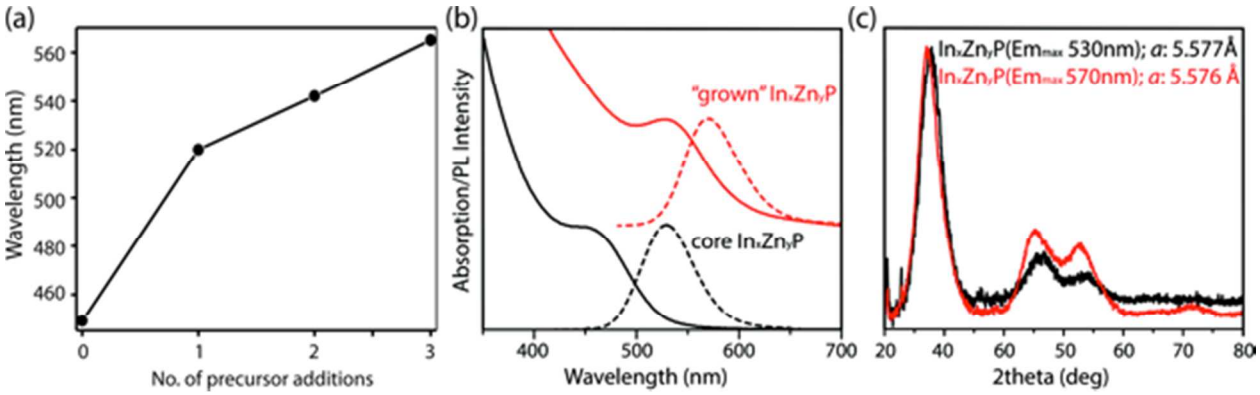

Figure S1. (a) Dependence of 1S absorbance wavelength on the number of In/Zn palmitate and $P(TMS)_3$ precursor additions. **(b)** Absorption and PL emission spectra of In_xZn_yP before and after further growth of the core by multiple injection of In-Zn and P precursor. For a Zn/In =1.5 ratio added in the synthesis, the Zn/In ratio measured with ICP was 0.68 in the small core, and slightly increased to 0.81 after further grow. **(c)** XRD pattern of In_xZn_yP before (black pattern) and after (red pattern) the further growth. The lattice constant of the two samples was roughly constant: 5.577 Å for In_xZn_yP before the growth and 5.576 Å for In_xZn_yP after the growth. Upon growth the cores retain roughtly the same Zn/In content and the same lattice constant.

TEM on InP (Zn/In = 0) before and after Ga CE reaction.

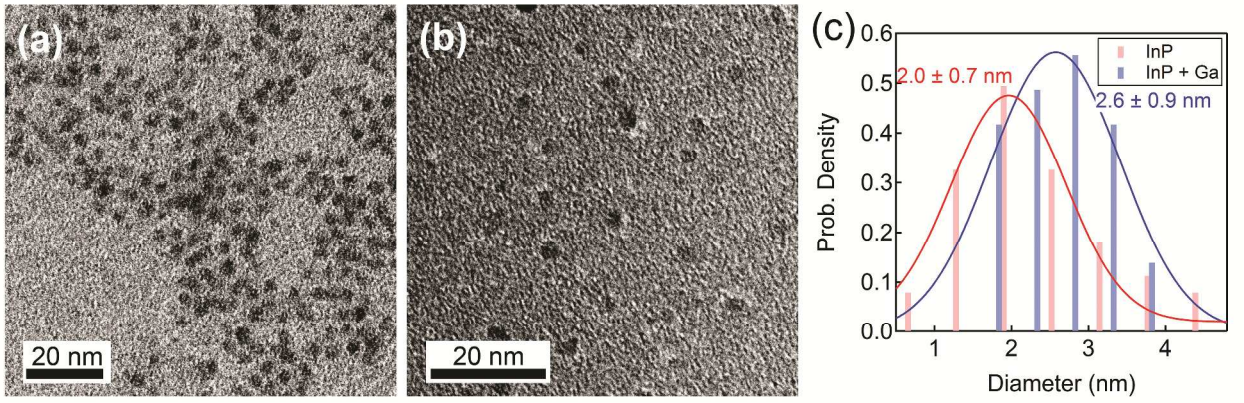

Figure S2. TEM images of InP QDs cores (Zn/In = 0) before **(a)** and after **(b)** the addition of 0.12 mmol $Ga(OA)_3$. Scale bar is 20 nm. (c) Histogram of QD diameters obtained from TEM images. The average particle size, determined from fits to the histograms, increased from 2.0 ± 0.7 in case of InP cores to 2.6 ± 0.9 after the addition of 0.12 mmol of $Ga(OA)_3$.

Extended data and controls for Ga CE reaction.

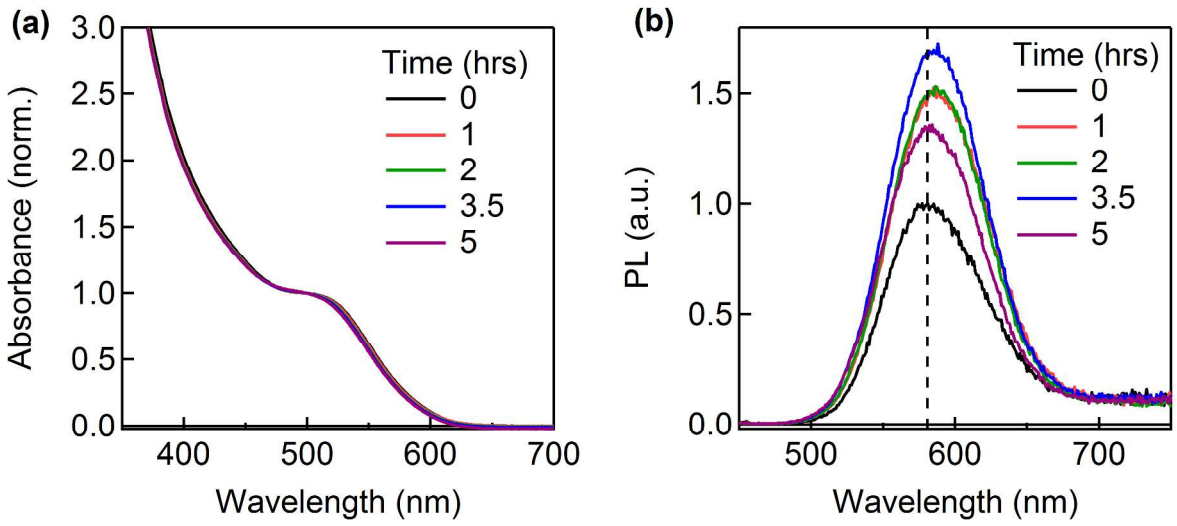

Figure S3. Effect of heating (200°C, 0-5 hours) on InZnP QDs (Zn/In = 1.0). **(a)** Absorbance spectra normalized to first exciton feature. The peak becomes more shoulder-like over time but otherwise there is little change. **(b)** PL spectra normalized to fraction of light absorbed at excitation wavelength (400 nm). The PL increases to 170% of its initial value over 3.5 hours but after this it decreases to 133% of the initial value.

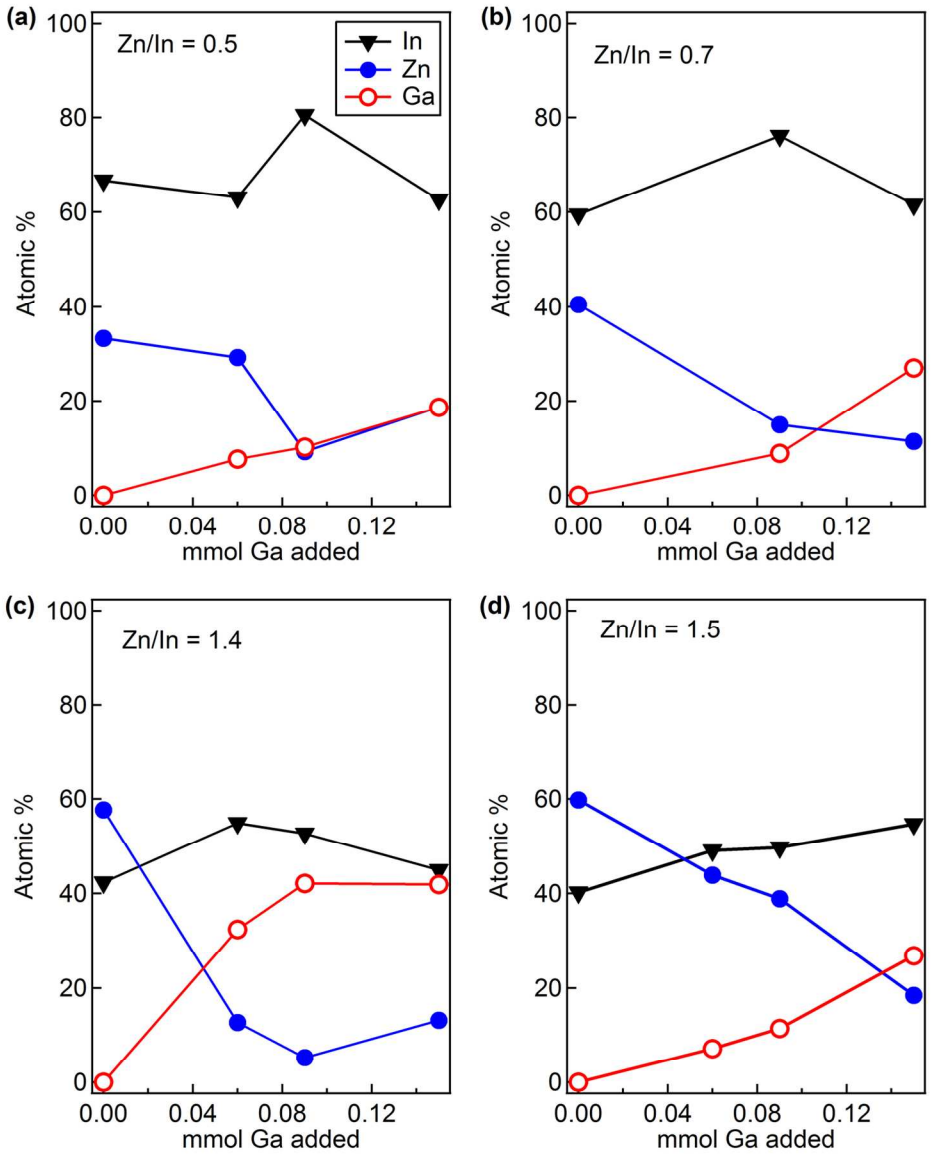

Figure S4. Data for additional reactions performed to reproduce the results of Figure 3 in the main paper. The composition of InZnP QDs is plotted as a function of added $Ga(OA)_3$, calculated from ICP measurements on reaction aliquots. **(a)** Zn/In = 0.5, **(b)** Zn/In = 0.7, **(c)** Zn/In = 1.4 and **(d)** Zn/In = 1.5. The data shows that similar quantitative results are seen for samples with similar Zn/In ratios, and that the trends discussed in the paper are reproducible.

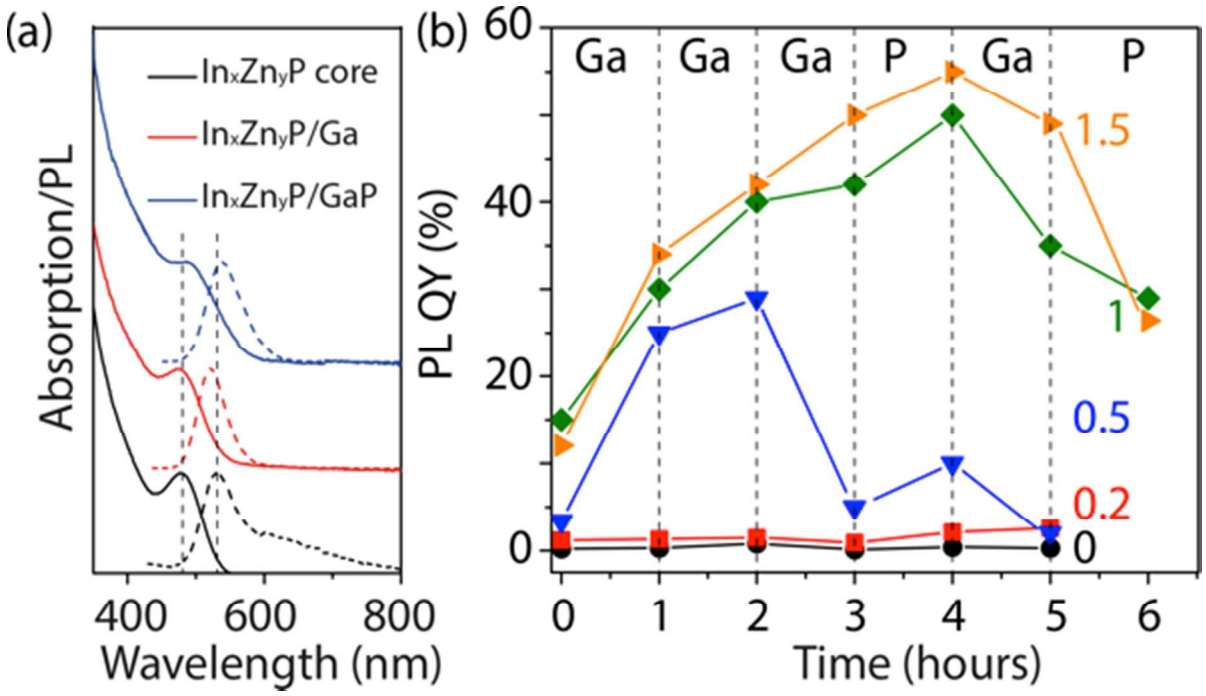

Figure S5. (a) Absorption and emission spectra of InZnP QDs (Zn/In = 1.5) at different stages during the growth of the GaP shell (each Ga and P addition was 0.03 mmol). **(b)** Plot of the PL QY InZnP/InGaP/GaP core/shell QDs with different initial Zn/In ratios (0, black curve; 0.2, red curve; 0.5, blue curve; 1, green curve; and 1.5, orange curve), as function of the amount of Ga and P precursor added during the growth of the GaP shell.

Extended data and characterisation of ZnSeS shell growth

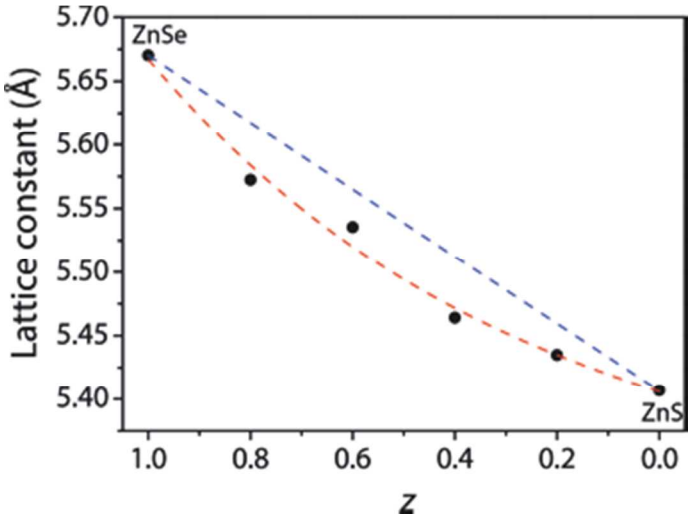

Figure S6. Plot of the lattice constant of the $ZnSe_zS_{1-z}$ shell as function of the composition *z*, as reported in reference 1.[1] Ideally, *z* varies from ZnSe to ZnS linearly via Vegard's law[2] (blue dashed line), but the trend can deviate from linearity by a bowing parameter (b),[3,4] according to equation (1):

$$y = (1 - z) * 5.406 + z * 5.670 - b * x * (1 - x) \qquad \text{(eq. 1)}$$

where 5.406 is the lattice constant of ZnS (Å) [1] and 5.670 is the lattice constant of ZnSe (Å).[1]

We fit the literature values (black dots) from reference 1 with equation (1) (red dashed curve), yielding a bowing parameter of 0.17 Å. This fit gives a direct correlation between the composition of the $ZnSe_zS_{1-z}$ shell and its lattice constant. We used the literature values[1] (black dots) to construct a continuous relationship between z and the lattice constant of $ZnSe_zS_{1-z}$ (red dashed curve) so that we can then extrapolate an *a* value for any given *z*.

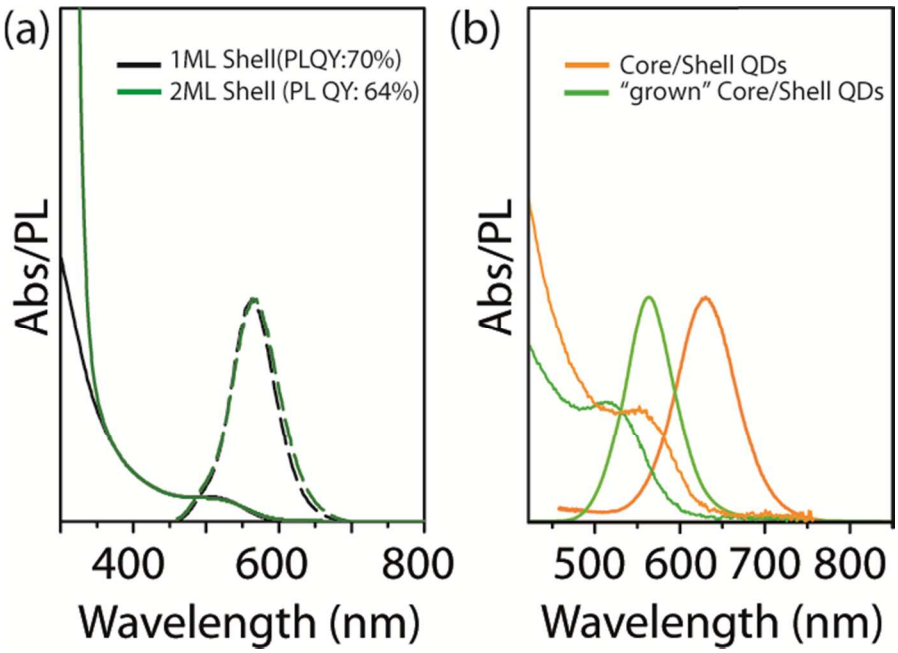

Figure S7. (a) Absorption and Emission spectra of In_xZn_yP/InGaP/GaP/$ZnSe_zS_{1-z}$ QDs with different shell thickness (1ML, black spectra and 2ML, green spectra). **(b)** Absorbance and emission spectra of InZnP/InGaP/GaP/$ZnSe_zS_{1-z}$ QDs emitting at 565 nm (green curve) and 627 nm (orange curve).

REFERENCES

(1) Sadekar, H. K.; Ghule, A. V.; Sharma, R. *J. Alloys Compd.* **2011**, *509* (18), 5525–5531.

(2) Denton, A.; Ashcroft, N. *Phys. Rev. A* **1991**, *43* (6), 3161–3164.

(3) Kats, A. *Indium Phosphide Relat. Mater. Process. Technol. Devices* **1992**, *Artech Hou*.

(4) Kuo, Y.-K.; Liou, B.-T.; Yen, S.-H.; Chu, H.-Y. *Opt. Commun.* **2004**, *237* (4-6), 363–369.