

Supporting Information

Gallium – a Versatile Element for Tuning the Photoluminescence Properties of InP Quantum Dots.

K. David Wegner,^{*a} Stéphanie Pouget,^b Wai Li Ling,^c Marie Carrière^d and Peter Reiss^{*a}

a. Univ. Grenoble Alpes, CEA, CNRS, INAC-SyMMES, 38000 Grenoble, France

b. Univ. Grenoble Alpes, CEA, CNRS, INAC-MEM, 38000 Grenoble, France

c. Univ. Grenoble Alpes, CEA, CNRS, IBS, 38000 Grenoble, France

d. Univ. Grenoble Alpes, CEA, CNRS, INAC-SyMMES, CIBEST, 38000 Grenoble, France

Experimental Section

Chemicals. Indium acetate (99.99%), zinc acetate (99.9%), gallium acetylacetonate (99.99%), anhydrous gallium chloride (99.99%), myristic acid (>99%), caprylic acid (>99%), propionic acid (>99%), tris(trimethylsilyl)phosphine (95%, (TMS)₃P), 1-octadecene (90%, ODE), 1-dodecanethiol (97%, DDT), dimethylformamide (DMF), toluene, methanol, chloroform, acetone and hexane were purchased from Sigma-Aldrich. Zinc stearate (90%, ZnSt₂) was acquired from Riedel de Haën. Oleic acid (>70%) came from Fisher Chemicals. All chemicals were used as received without any further purification unless stated otherwise.

Zinc xanthate was prepared according to the procedure reported in Ref. 1.

Preparation of indium myristate. Indium acetate (6.9 mmol), myristic acid (21.4 mmol) and ODE (15 mL) were mixed in a 50 mL three neck flask. The solution was stirred and degassed under vacuum for 3 hours at 120°C. After cooling down to room temperature the precipitated indium myristate was washed with around 150 mL of anhydrous hexane before drying under vacuum.

Typical synthesis of NCs using gallium oleate. Indium myristate (0.1 mmol), ZnSt₂ (0.1 mmol) and 7.5 mL ODE were mixed in 50 mL three-neck flask and degassed for one hour. Separately, gallium chloride (0.07 mmol), oleic acid (0.25 mmol) (or caprylic acid, propionic acid) and 1 mL 1-octadecene were mixed in a 4 mL vial and heated to 80-90°C under stirring until a clear solution was obtained. The first flask was backfilled with Ar and the gallium precursor solution added. It is unlikely that all three chloride ions of GaCl₃ are substituted using this procedure. In the molten state (above 78°C), gallium chloride forms dimeric molecules Ga₂Cl₆, which undergo substitution reactions with carboxylic acids. However, replacement of the bridging chlorides requires very harsh reaction conditions (cf. Ref. 2). Therefore, “gallium oleate” signifies here species of the formula [GaCl_x·(C₁₇H₃₃COO)_{3-x}]₂ (x=1...2), i.e. with maximum two Cl ions substituted per Ga. The reaction mixture was rapidly heated to 300°C in a molten salt bath and at 100°C 0.1 mmol (TMS)₃P, dissolved in 1 mL ODE, were swiftly injected. After 30 min, the reaction was quenched by removing the salt bath and let cool down to room temperature. The NCs were purified three times using a precipitation (addition of 2 mL of a 1:1 v/v mixture of methanol/chloroform followed by 10 mL of acetone) and redispersion (in 5 mL of chloroform) cycle and finally stored in hexane.

Typical synthesis of NCs using gallium acetylacetonate. 0.02 mmol gallium acetylacetonate, 0.1 mmol indium-myristate, 0.2 mmol ZnSt₂, 0.1 mmol DDT and 8.5 mL of ODE were mixed in a 50 mL three neck flask. The reaction mixture was degassed under vacuum for 1 hour and backfilled with Ar before rapidly heating up to 300°C in a molten salt bath. At around 100°C 0.1 mmol of (TMS)₃P, dissolved in

1 mL ODE, were swiftly injected. After 30 min, the reaction was quenched by removing the salt bath and cooling the solution down to room temperature. The NCs were purified as described for the synthesis with gallium oleate.

Post-synthetic treatment using gallium oleate. The NCs synthesis using gallium acetylacetonate was performed as before but instead of cooling down to room temperature the temperature was kept at 200°C using a heating mantle. 50 µL of a freshly prepared gallium oleate solution (0.16 mmol GaCl₃ + 3.1 mmol oleic acid + 5 mL ODE) was added and the solution stirred for one hour. Then the reaction was stopped, and the NCs were purified as described before.

Passivation of the NCs with a ZnS shell. The synthesis of the NCs was performed like described above but instead of cooling down to room temperature the solution was kept at a temperature of 230°C using a heating mantle. A shell precursor solution consisting of 0.1 mmol zinc xanthate dissolved in 100 µl DMF and 1mL toluene was mixed with 0.8 mmol of ZnSt₂ dissolved in 3 mL ODE and then injected to the core NCs using a syringe pump with a pump rate of 8 mL/h. After 40 min the reaction was cooled down to room temperature and purified as described before.

In(Zn)P NCs synthesis. The synthesis of In(Zn)P NCs, used as reference in this work, was carried out as described for the typical synthesis of NCs using gallium oleate but omitting the addition of the gallium precursor.

Sample characterization

Photophysical characterization. Absorbance measurements were performed using a Hewlett Packard 8452A spectrophotometer whereas the emission spectra were recorded using a Fluorolog FL3-22 spectrometer from Horiba-Jobin Yvon equipped with a 150 W xenon lamp for steady-state measurements and a NanoLED laser diode from Horiba with a wavelength of 350 nm and 1 MHz repetition for time-resolved measurements. Decay curves were fitted using Decay Analysis software from Horiba Scientist. Amplitude and intensity weighted average decay times were calculated according to equation 1 and 2, respectively.

$$\tau < amp > = \frac{\sum_i A_i \tau_i}{\sum_i A_i} \quad (1)$$

$$\tau < int > = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i} \quad (2)$$

In equation 1 and 2 A_i is the amplitude of the respective decay time τ_i . Photoluminescence quantum yield measurements were performed at room temperature using an integration sphere, Hamamatsu Quantaaurus Absolute PL quantum yield spectrometer.

Structural characterization. Powder X-ray diffraction pattern was obtained using a Panalytical X'Pert powder diffractometer equipped with copper anode ($\lambda_{K_{\alpha 1}}=1.5406$ Å, $\lambda_{K_{\alpha 2}}=1.5444$ Å) and an X' Celerator 1D detector. The elemental composition was analysed using a Zeiss Ultra 55+ scanning electron microscope equipped with an EDX probe. The XRD and EDX samples were prepared by drop-casting a concentrated NCs dispersion either on a disoriented silicon substrate or on a cleaned silicon substrate. Around 4 mL diluted sample was applied onto a 400-mesh copper transmission electron microscopy grid covered with a homemade carbon film and the solvent was allowed to evaporate. Transmission electron microscopy was performed at cryogenic temperature on an FEI Polara microscope operating at 300 kV and images were recorded on a Gatan K2 camera.

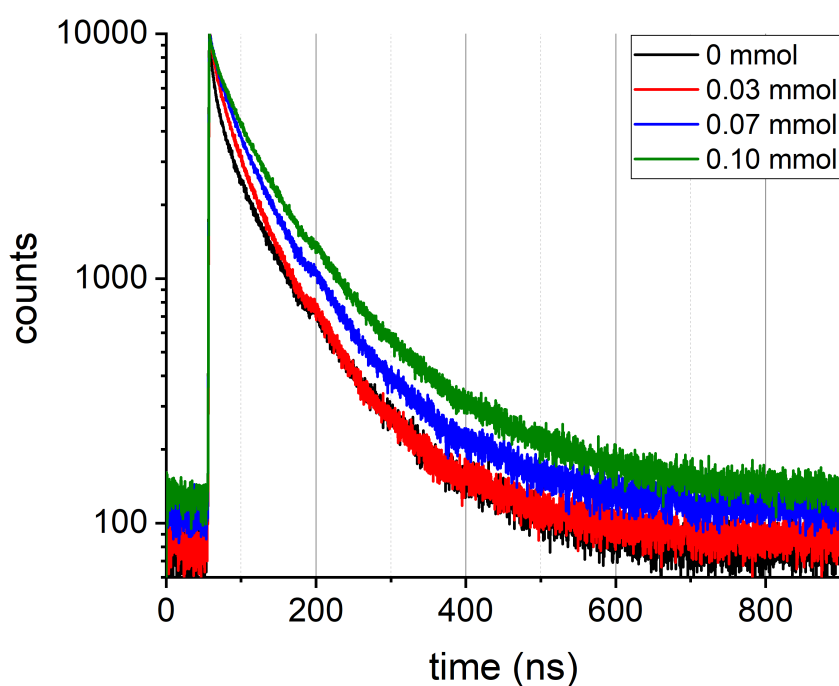
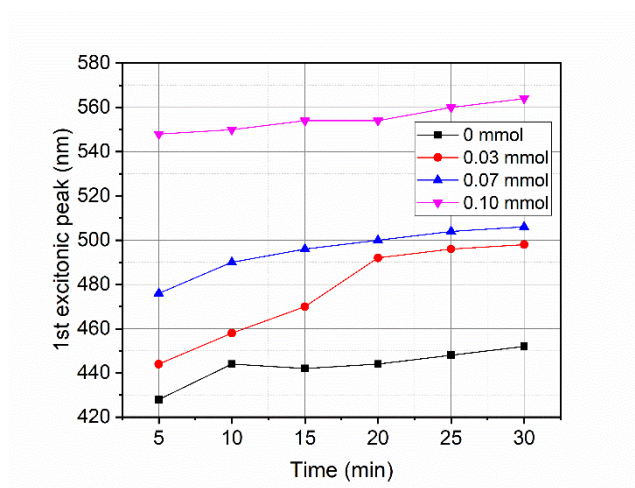


Figure S1: Photoluminescence (PL) decay curves using increasing amounts of gallium oleate precursor.

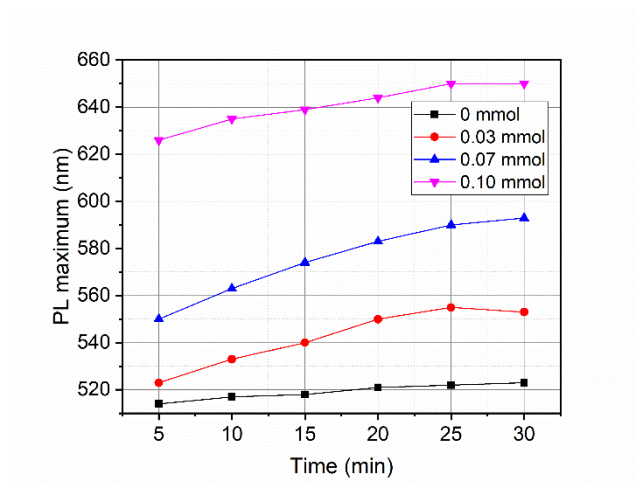
Table S1: Evaluation of the PL decay curves with increasing gallium oleate concentrations using a triexponential fit.

mmol	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	τ_{amp} (ns)	τ_{int} (ns)
0	6.1	4.1	31.1	31.1	62.8	92.2	67.8	83.2
0.03	5.5	6.9	43.2	34.9	51.3	89.5	61.4	75.6
0.07	3.2	6.9	36.3	37.3	60.6	93.9	70.6	82.8
0.10	2.0	5.9	37.7	44.5	60.3	113.0	85.0	99.3

A)



B)



C)

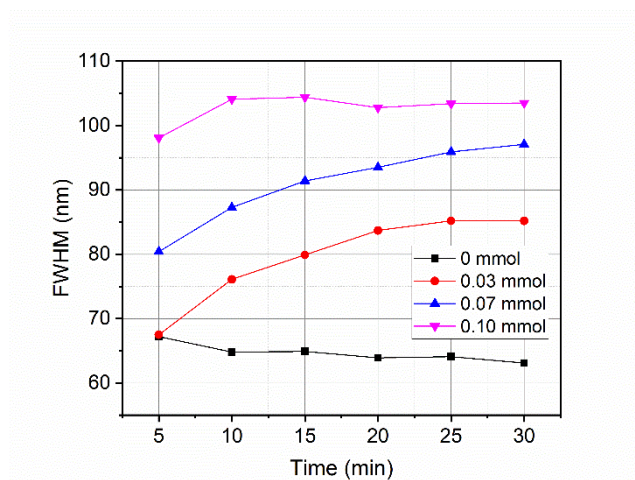


Figure S2: Position of the 1st excitonic peak (A), the PL maximum (B) and PL linewidth (C) measured at different time intervals during the synthesis of InP NCs with increasing concentrations of gallium oleate (prepared from GaCl_3).

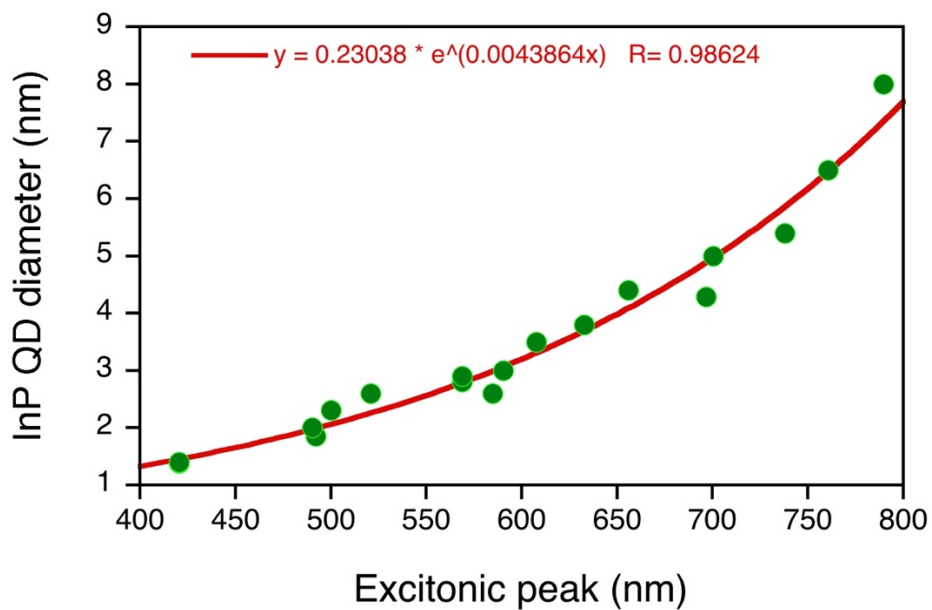


Figure S3: Sizing curve for InP NCs correlating the NC diameter with the 1st excitonic peak of the absorbance spectrum. The green data points have been extracted from references 3-5.

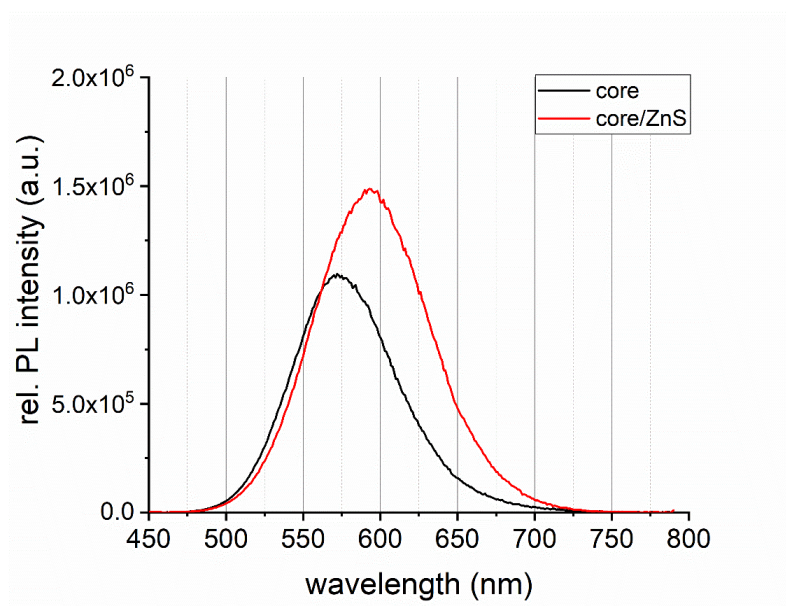


Figure S4: Absorbance corrected PL spectra of core InP NCs using 0.03 mmol gallium oleate (black) and after the epitaxial growth of a ZnS shell on the same core (red).

Table S2: Peak positions from the X-ray diffractograms of InP NCs with increasing gallium oleate concentration.

Gallium [mmol]	Pos. [$^{\circ}2\theta$] - 111	Pos. [$^{\circ}2\theta$] - 220	Pos. [$^{\circ}2\theta$] - 311
0	26.4	44.2	51.9
0.03	26.3	43.8	51.8
0.07	26.4	43.9	51.8

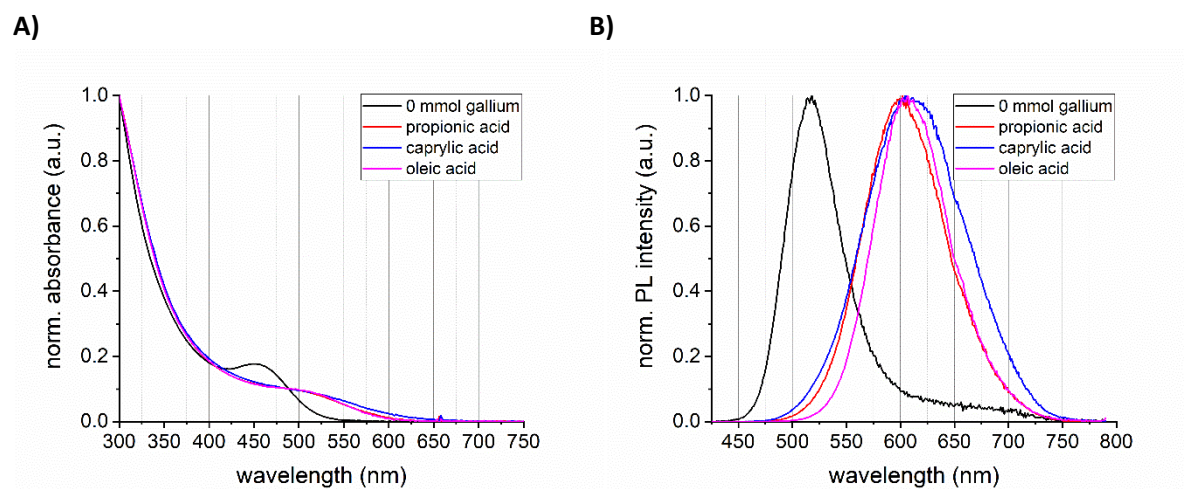
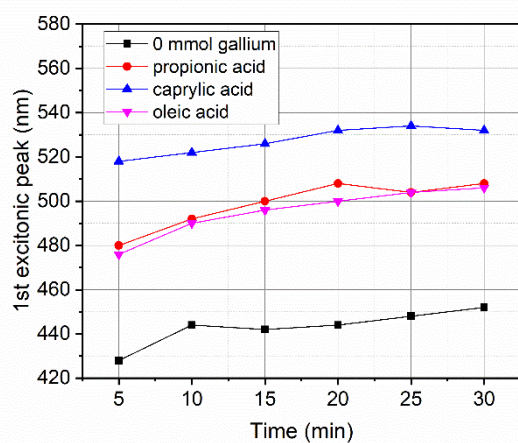
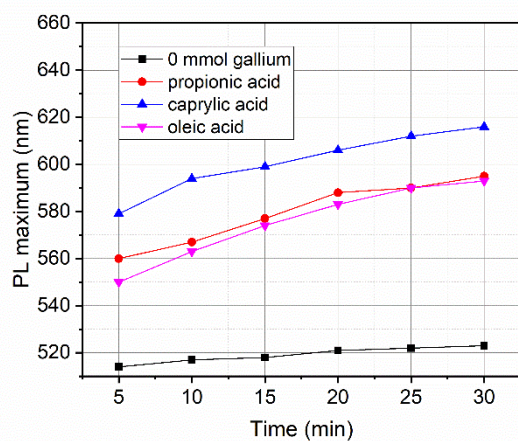


Figure S5: Comparison of the normalized absorbance (**A**) and PL spectra (**B**) for InP NCs synthesized without the addition of a gallium precursor (black) and with addition of 0.07 mmol gallium chloride dissolved in either propionic acid (red) or caprylic acid (blue) or oleic acid (magenta).

A)



B)



C)

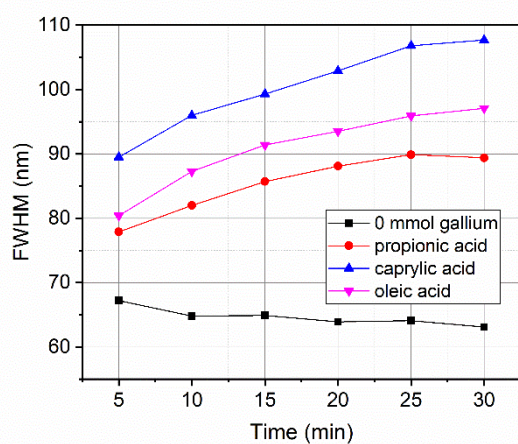


Figure S6: Position of the 1st excitonic peak (A)), the PL maximum (B)) and PL linewidth (C)) measured at different time intervals during the synthesis of InP NCs synthesized without the addition of a gallium precursor (black) and with addition of 0.07 mmol gallium chloride dissolved in either propionic acid (red) or caprylic acid (blue) or oleic acid (magenta).

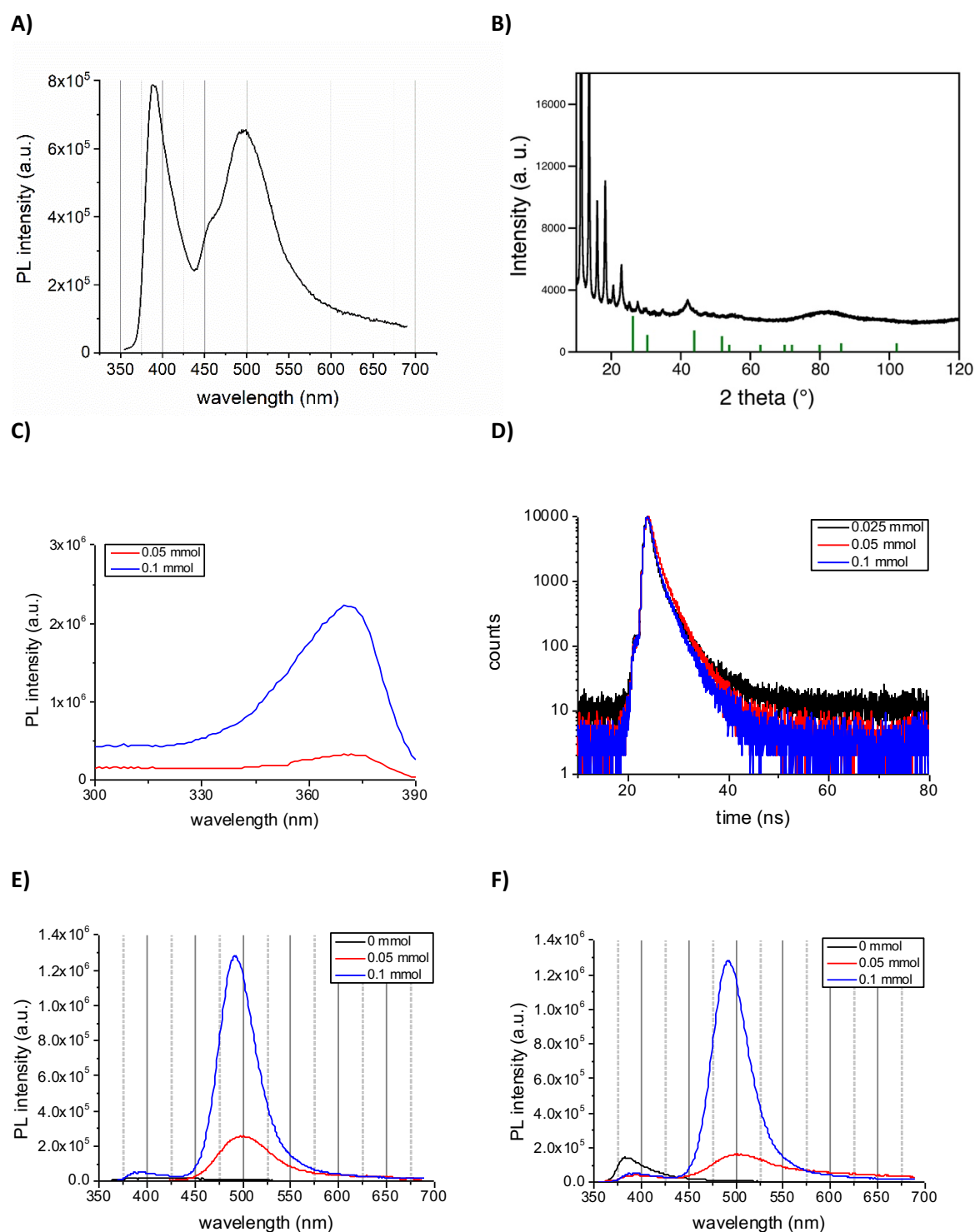


Figure S7: A) PL spectrum of InP NCs synthesis using 0.1 mmol Ga(acac)₃ (In myristate, Zn stearate, PTMS: 0.1 mmol). B) Powder X-ray diffractogram of the unidentified phase (green bars: reference pattern of zinc blende indium phosphide (JCPDS #32-0452). C) PLE spectra (emission wavelength: 395 nm) for two different Ga concentrations. D) TRPL spectra (emission wavelength: 390 nm); for all samples amplitude averaged decay times in the range of 1.1-1.5 ns are obtained. E) Influence of the indium myristate concentration (Zn stearate: 0.1 mmol); F) influence of the zinc stearate concentration (In myristate: 0.1 mmol) on the formation of the 390 nm emission peak (reaction time: 20 min, Ga(acac)₃: 0.025 mmol). Decreasing the amount of indium myristate and increasing the amount of zinc stearate reduces the contribution of the 390 nm emitting species.

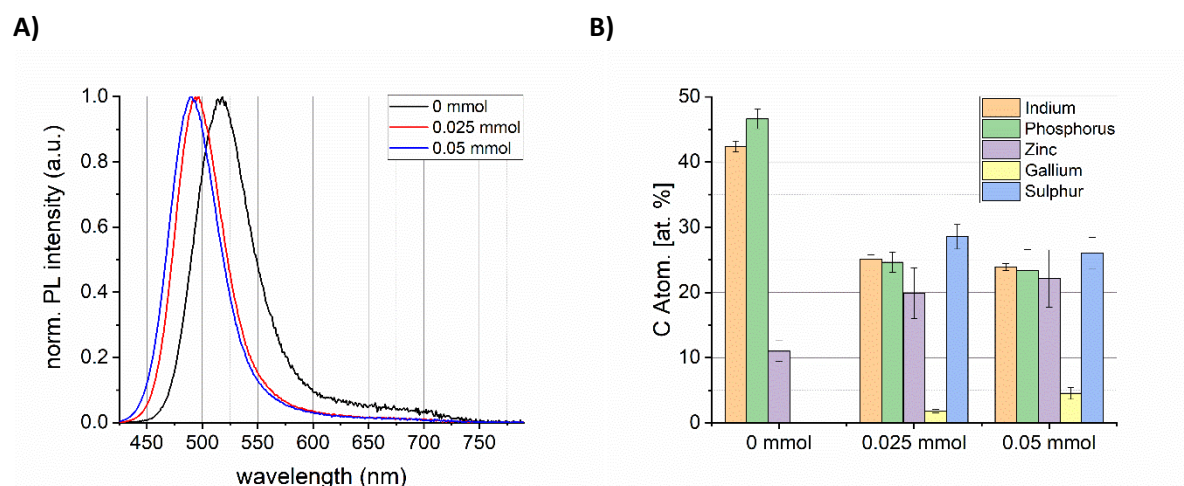


Figure S8: Comparison of the normalized PL spectra (**A**) and results of the elemental analysis (**B**) for InP NCs synthesized with increasing concentrations of Ga(acac)₃ (in presence of 0.1 mmol of DDT). In the case of 0.025 mmol Ga precursor added, the 1:10 Ga:In ratio obtained after synthesis corresponds to 4-5 Ga ions per QD; in the case of 0.05 mmol, the Ga:In ratio is 1:5 corresponding to approximately 10 Ga ions per QD.

Table S3: Comparison of the position of the 1st excitonic peak (Abs. max), Photoluminescence maximum (PL. max.) and the full width at half maximum (FWHM) for InP NCs synthesised without addition of gallium (gallium free), 0.03 mmol gallium oleate and 0.025 mmol Ga(acac)₃.

sample	Abs. max (nm)	PL max. (nm)	FWHM (nm)
gallium free	450	518	59.4
gallium oleate	490	572	77.1
Ga(acac) ₃	434	494	52.6

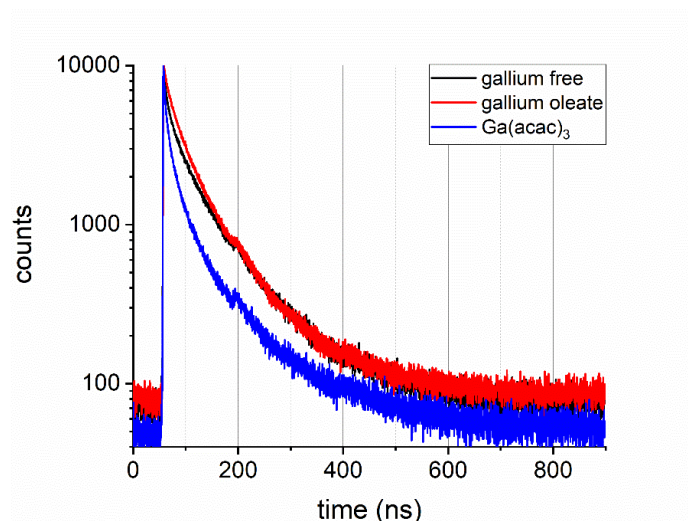


Figure S9: Comparison of PL decay curves of InP NCs synthesized without gallium (black), using 0.03 mmol gallium oleate (red) and using 0.025 mmol Ga(acac)₃.

Table S4: Evaluation of the PL decay curves of InP NCs without the addition of gallium precursor (gallium free), with the addition of 0.03 mmol gallium oleate (gallium oleate) and with addition 0.025 mmol gallium acetylacetonate ($\text{Ga}(\text{acac})_3$) using a triexponential fit.

	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	$\tau_{\text{<amp>}}$ (ns)	$\tau_{\text{<int>}}$ (ns)
gallium free	6.1	4.1	31.1	31.1	62.8	92.2	67.8	83.2
gallium oleate	5.5	6.9	43.2	34.9	51.3	89.5	61.4	75.6
$\text{Ga}(\text{acac})_3$	10.6	2.6	39.7	20.9	49.7	93.7	55.1	82.3

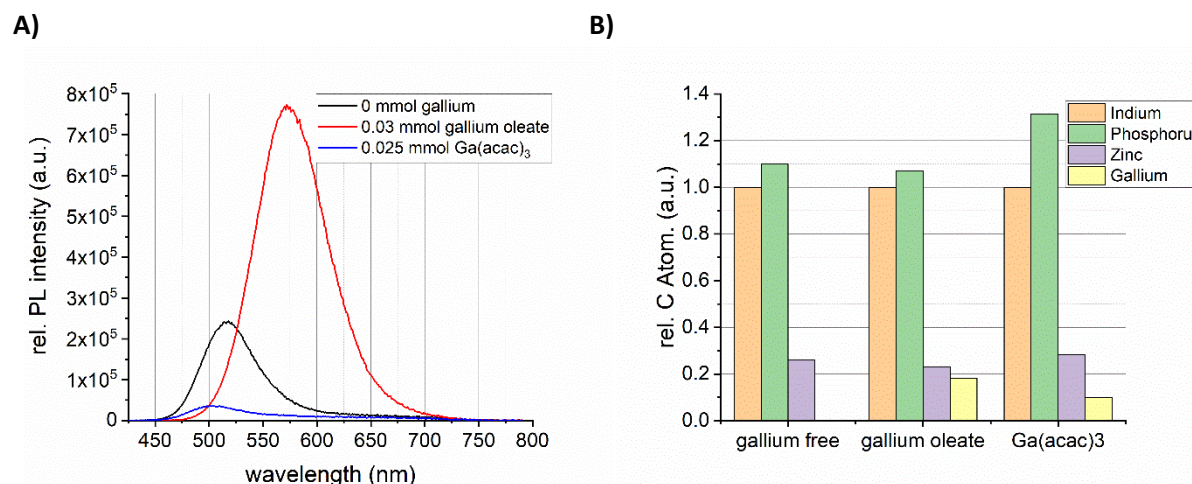


Figure S10: **A)** Absorbance corrected PL spectra of InP NCs without the addition of gallium precursor (black), with addition of 0.03 mmol gallium oleate (red) and with addition 0.025 mmol gallium acetylacetonate (blue, $\text{Ga}(\text{acac})_3$). **B)** On Indium normalized elemental analysis of InP NCs without the addition of gallium precursor (gallium free), with the addition of 0.03 mmol gallium oleate (gallium oleate) and with addition 0.025 mmol gallium acetylacetonate ($\text{Ga}(\text{acac})_3$).

Table S5: Peak position, FWHM and the calculated size using the Scherrer equation from the XRD spectra of InP NCs without the addition of gallium precursor (gallium free), with the addition of 0.03 mmol gallium oleate (gallium oleate) and with addition 0.025 mmol gallium acetylacetonate ($\text{Ga}(\text{acac})_3$).

sample	Pos. [$^{\circ}2\theta$] - 111	Pos. [$^{\circ}2\theta$] - 220	Pos. [$^{\circ}2\theta$] - 311	size (nm)
gallium free	26.4	44.2	51.9	1.7(2)
gallium oleate	26.3	43.8	51.8	1.7(2)
$\text{Ga}(\text{acac})_3$	27.4	45.6	53.0	1.4(2)

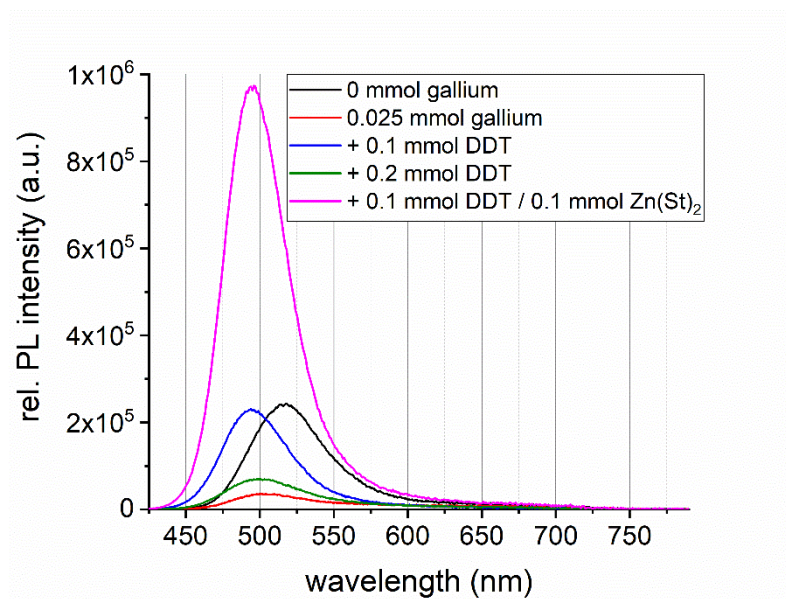


Figure S11: Absorbance corrected PL spectra of InP NCs with 0.025 mmol $\text{Ga}(\text{acac})_3$ with increasing concentrations of DDT and $\text{Zn}(\text{St})_2$.

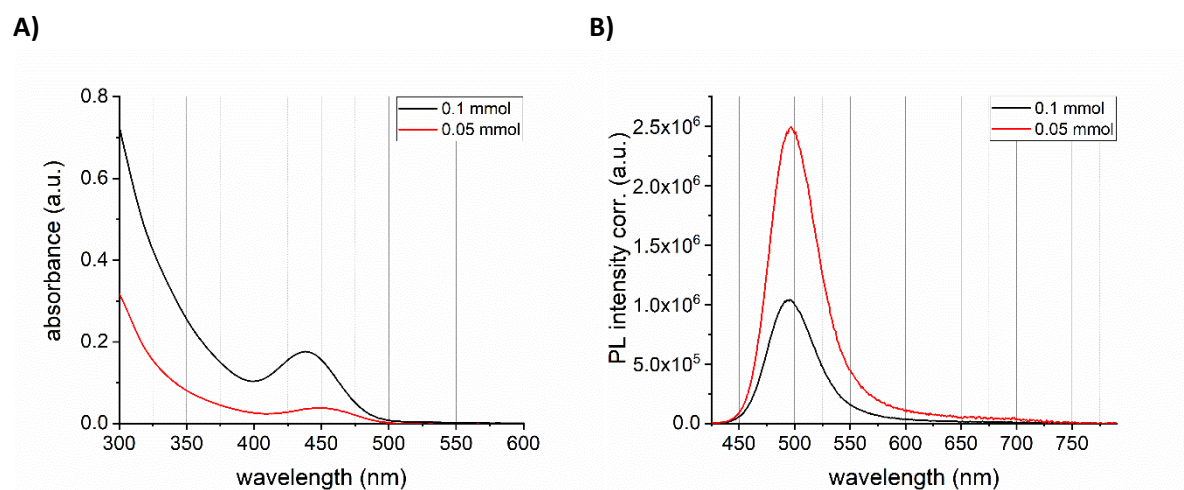


Figure S12: Absorbance spectra (A) and absorbance corrected PL spectra (B) of InP NCs synthesized with 0.025 mmol $\text{Ga}(\text{acac})_3$ and using two different concentrations of the phosphorus precursor $(\text{TMS})_3\text{P}$.

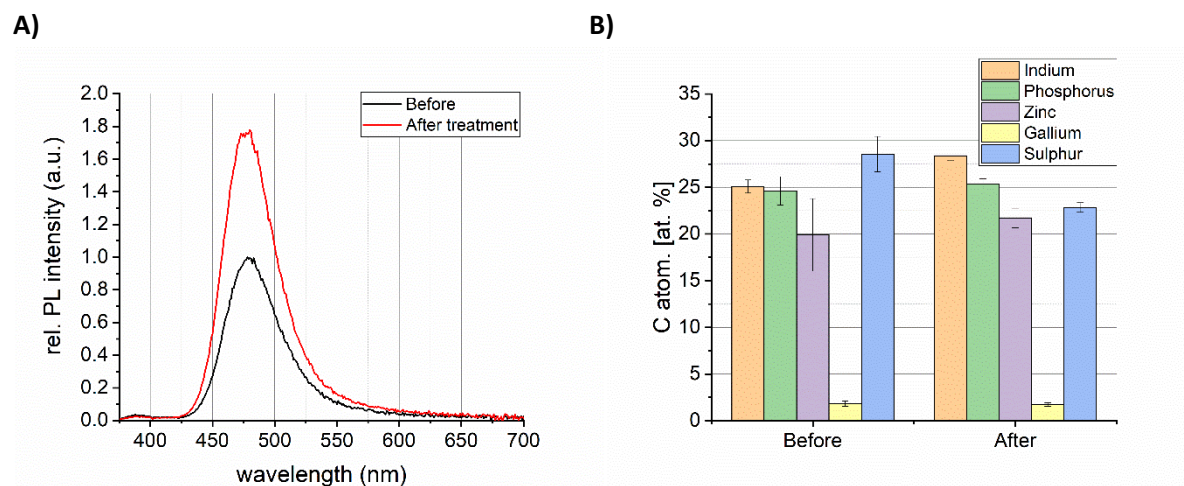


Figure S13: Relative PL spectrum and elemental analysis of InP NCs synthesized with 0.025 mmol Ga(acac)₃ before and after a 60 min. post-synthetic treatment with gallium oleate.

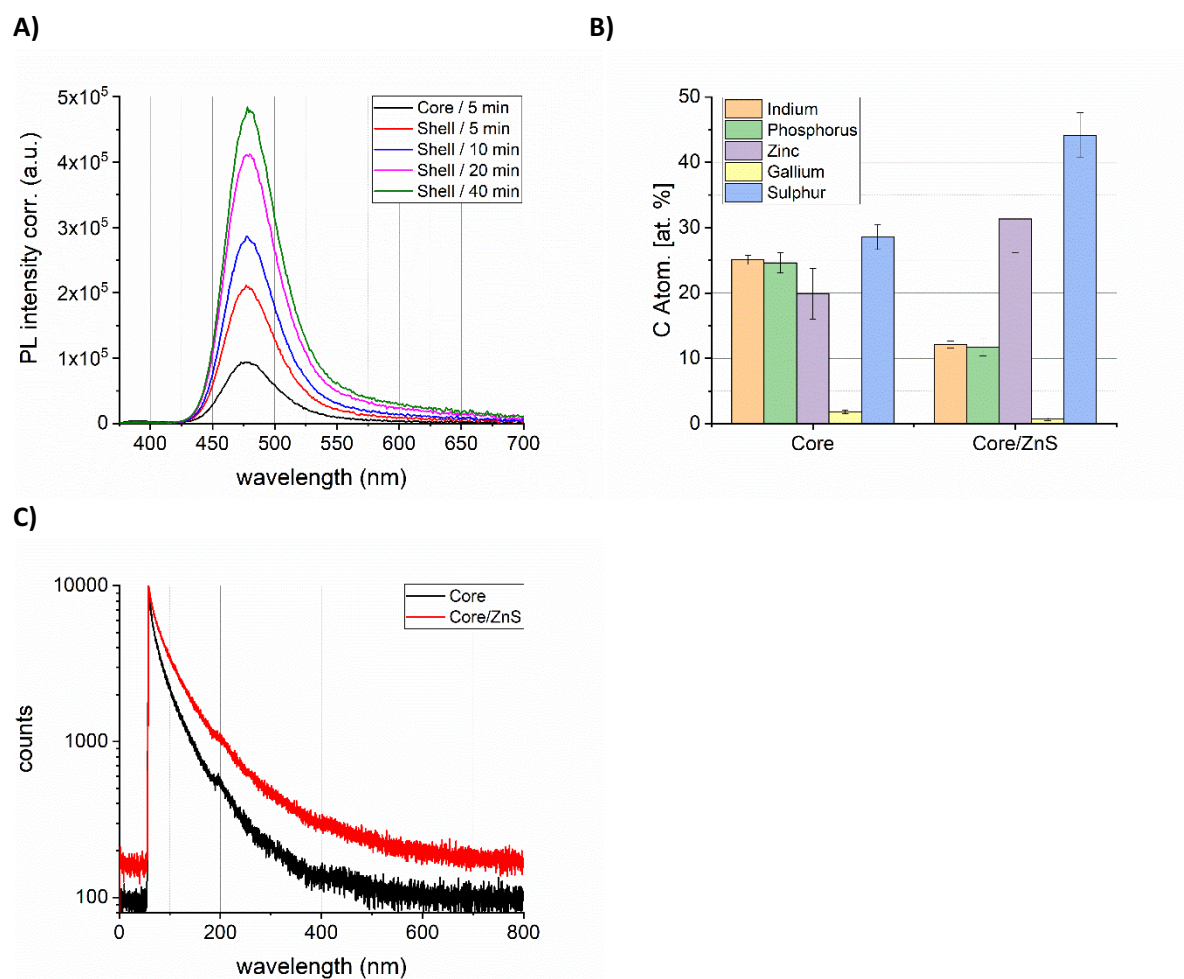


Figure S14: **A)** Absorbance corrected PL spectra of aliquots taken at different times during the synthesis of a ZnS shell around a InP NCs synthesized with 0.025 mmol Ga(acac)₃. **B)** Elemental analysis of the InP NCs synthesized with 0.025 mmol Ga(acac)₃ before and after ZnS shell growths. **C)** Comparison of PL decay curves before and after ZnS shell growth.

Table S6: Evaluation of the PL decay curves of core and core/ZnS NCs using a triexponential fit.

	A ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	A ₃	τ ₃ (ns)	τ<amp> (ns)	τ<int> (ns)
Core	5.0	2.9	31.4	21.8	63.6	73.2	53.5	66.4
Core/ZnS	4.3	6.1	38.8	38.5	56.9	108.8	77.1	94.8

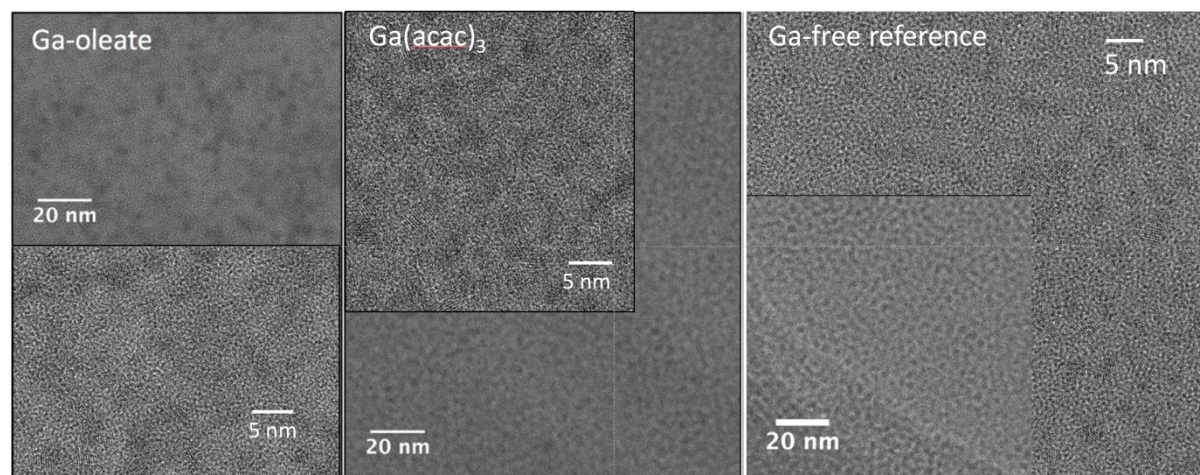


Figure S15: TEM images of InP NCs synthesized with 0.07 mmol gallium oleate and with 0.05 mmol Ga(acac)₃ as well as the Ga-free In(Zn)P reference. Mean sizes are 3.03±0.57, 2.01±0.21 nm and 2.67±0.32, respectively.

References:

- 1) M. Protière, P. Reiss, *Nanoscale Res. Lett.* 2006, **1**, 62-67.
- 2) H. Funk and A. Paul, *Z. Anorg. Allg. Chem.*, 1964, **330**, 70-77.
- 3) O. I. Micic, C. J. Curtis, K. M. Jones, J. R. Sprague, A. J. Nozik, *J. Phys. Chem.* 1994, **98**, 4966-4969.
- 4) H. Fu, A. Zunger, *Phys. Rev. B* 1997, **56**, 1496-1508.
- 5) D. V. Talapin, N. Gaponik, H. Borchert, A. L. Rogach, M. Haase, H. Weller, *J. Phys. Chem. B* 2002, **106**, 12659-12663.