# The Role of Water in the Synthesis of Indium Nanoparticles

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## **Experimental**

InCl<sub>3</sub> (anhydrous, 99.999%), oleylamine (technical, 70%), *n*-butylamine (99.5%), phenylsilane (97%) were purchased from Sigma Aldrich. Octylsilane was purchased from Fluorochem. THF and EtOH were purchased from Carlo Erba and dried using an MBraun Solvent Purifying system SPS 800. *N*-butylamine was dried on 4Å molecular sieves. The water content was titrated using a Karl Fisher apparatus (120 ppm water was measured after the drying procedure).

All reactions were routinely performed under an inert atmosphere of argon or nitrogen using standard Schlenk and glovebox techniques.

*Safety note:* White phosphorus is stable in water but highly flammable and toxic if swallowed or inhaled. It is incompatible with oxidizing agents, reducing agents and bases. It is light and heat sensitive. It should be handled accordingly.

## **Optimized synthesis of 7 nm In NPs**

166 mg InCl<sub>3</sub> (0.75 mmol) were weighed in a 100 mL Schlenk inside a N<sub>2</sub>-filled glovebox. 1 mL drieddegassed oleylamine (3 mmol) was added. Outside the glovebox, 12 mL dried, degassed butylamine was added as well as 30  $\mu$ L of deionized water (1.7 mmol). After all of the InCl<sub>3</sub> was dissolved (5 min of stirring), the LiBH<sub>4</sub> solution was added (1.1 mL, 2M solution in THF, 2.2 mmol). The mixture was left to stir for 15 min at room temperature and then put in a 70 °C oil bath for 10 min. After 2 min, the mixture turns yellow, then brown, then dark brown. The reaction was quenched by putting the Schlenk in a water bath at room temperature and by addition of 30 mL EtOH. The NPs were left to precipitate and the light brown supernatant was discarded by canula filtration. The NPs were dried under vacuum, redispersed in oleylamine and transferred to a centrifugation tube inside a glovebox. After 5 min at 3000 rpm, the supernatant containing only 7 nm NPs was transferred to a Schlenk for further reaction.

#### Study of the influence of water content.

41.5 mg InCl<sub>3</sub> (0.19 mmol) were weighed in a 20 mL Schlenk inside a N<sub>2</sub>-filled glovebox. 250  $\mu$ L drieddegassed oleylamine (0.75 mmol) was added. Outside the glovebox, 3 mL dried, degassed, *N*-butylamine (120 ppm water) was added. 3.4, 6.8, 10.5, 13.4, 17.0  $\mu$ L deionized water (0 to 5 equiv) were added using a microsyringe. After all of the InCl<sub>3</sub> was dissolved, the LiBH<sub>4</sub> solution was added (0.28 mL, 2M solution in THF, 0.55 mmol). The mixture was left to stir for 15 min at room temperature and then put in a 70 °C oil bath for 10 min. The reaction was quenched by putting the Schlenk in a water bath at room temperature and by addition of 7.5 mL EtOH. The solution was then transferred to a centrifugation tube, the particles isolated and precipitated again using a mixture of EtOH and THF, and analyzed by TEM.

#### **Transformation to InP NPs**

To the solution of 7 nm In NPs were added 1.5 mL of a 0.5 M  $P_4$  solution in toluene (0.75 mmol) and 145  $\mu$ L of octylsilane (0.75 mmol). The mixture is heated at 90 °C for 4 hours and then to 110 °C for 2 hours. Nanoparticles are precipitated by centrifugation three times by addition of THF and EtOH for characterization.

# **X-Ray Powder Diffraction**

X-Ray powder diffractograms were recorded on a PANalytical X'Pert Pro  $\theta$  using a Cu source (wavelength: 1.5418 Å) and a linear X'Celerator detector. The diffractometer was used in Bragg-Brentano configuration with Soller front slits (0.04 rad) and divergence slits coupled with a filter to insure a constant length of irradiation of 10 mm. Data were recorded with 20 between 2 and 90° (step: 0.016°, 1000 s per step). Samples were deposited on a Si holder. Crystallite sizes were calculated using the Scherrer Calculator tool of the Highscore software.

Scherrer formula:

Crystallite size (average) = k \*  $\lambda / (B_{size} \cos \theta)$ 

With:

• 
$$B_{size} = \sqrt{B_{obs}^2 - B_{std}^2}$$

- $B_{obs} = FWHM$  of the sample
- $B_{std} = FWHM \text{ of a standard } (LaB_6)$
- k = 0.9 (spherical approximation)
- $\lambda = 1.5418 \text{ Å}$

## **Transmission Electron Microscopy**

Samples were prepared by depositing a drop of a THF solution of NPs on a copper grid. The images were recorded on a JEOL JEM 1400 TEM. EDX was performed on a JEOL JEM-ARM-200F.

# **Analysis of TEM images**

TEM images were analyzed using ImageJ software: Areas of NPs were collected and the diameter was determined by assuming that the NPs are spherical.



Figure S1: TEM image and size distribution of the optimized In NPs. Average diameter: 6.8 ± 0.7 nm (870 particles analyzed).



Figure S2: TEM images and size distribution of InP NPs. Average diameter:  $5.9 \pm 0.9$  nm (763 particles analyzed).

The average diameter calculated in the case of InP NPs must however be taken with caution. Indeed, the InP are less contrasted and spherical than the In NPs, which makes the analysis less precise.

# Reaction between In NPs and P<sub>4</sub> at 130°C



Figure S3: TEM picture of InP NPs after reaction with P<sub>4</sub> at 130 °C for 2 h; (B) corresponding XRD pattern

# Reaction between In NPs and P<sub>4</sub> at 90°C



Figure S4: NPs after reaction with P<sub>4</sub> at 90 °C for two hours. (A) EDX 1: TEM image of mixture of 7- and 20-25nm NPs; 2: mapping of phosphorus; 3: mapping of In. (B) XRD pattern of the mixture



Figure S5: quantitative EDX analysis of a large InP nanoparticle after reaction with P<sub>4</sub> at 90 °C showing an In:P ratio of 53.6:46.4



Figure S6: quantitative EDX analysis of a large InP nanoparticle after reaction with  $P_4$  at 90 °C showing an In:P ratio of 73:27.



Figure S7: quantitative EDX analysis of a small In nanoparticle after reaction with P4 at 90 °C



Figure S8: quantitative EDX analysis of numerous small In NPs after reaction with P4 at 90 °C



Figure S9: XRD pattern of the NPs after reaction between the 7-nm and  $22\pm4$  nm In NPs with P<sub>4</sub> at 90 °C.

# IR spectrum of the solid sample

2 mg of powder of In NPs was mixed with KBr to form a pellet, that was then analyzed on a 6700 Thermoscientific IR spectrometer (Transmission mode, detector: DLaTGS, resolution 4cm<sup>-1</sup>, 16 scans)



Figure S10: FTIR spectrum of KBr-In NPs pellet

### <sup>31</sup>P NMR Spectra

Nuclear magnetic resonance spectra were recorded on a Bruker AC-300 SY spectrometer operating at 121.5 MHz for  ${}^{31}P$ ; chemical shifts are relative to an 85% H<sub>3</sub>PO<sub>4</sub> external reference.



Figure S11: <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the reaction between In NPs and P<sub>4</sub> at 130 °C in oleylamine: A) initially; B) After 2 hours at 130 °C. PPh<sub>3</sub> is used as an internal standard.



Figure S12: <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the reaction between  $P_4$  NPs and OctSiH<sub>3</sub> at 120 °C in oleylamine: A) initially; B) After 1 hour at 160 °C. PPh<sub>3</sub> is used as an internal standard.