Supplementary Material (ESI) for Chemical Communications


# Supporting Information

# White phosphorus and metal nanoparticles: a versatile route to metal phosphide nanoparticles

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## 1. General Procedures

All reactions were carried out under nitrogen atmosphere using standard air-free techniques.[1] All reagents and chemicals were obtained commercially and used as received. Dry THF was obtained by distillation from Na/benzophenone. Dry toluene was distilled on Na.

Powder XRD measurements were performed with a Bruker D8 X-ray diffractometer operating in the reflection mode at Cu Kα radiation with 40 kV beam voltage and 40 mA beam current. The data were collected in the 20-80° range (2θ) with steps of 0.03° and a counting time of at least 3 s.

Transmission Electron Microscopy (TEM): Samples were prepared by evaporating a drop of hexane diluted suspension of the nanoparticles on a carbon-coated copper grid. The nanoparticles were studied using a Philips CM30 (300 kV) apparatus and a TECNAI 120 (120 kV) apparatus. Elemental analysis was performed by energy-dispersive X-ray spectroscopy (EDS) on a Hitachi S-3600N scanning electron microscope.

NMR spectra were recorded on a Bruker AMX-300 spectrometer. $^{31}P$ chemical shifts are relative to a 85% $H_3PO_4$ external reference.

## 2. Synthetic procedures

### 2.1 Synthesis of 'small' InP nanoparticles

Preparation of In nanoparticles: 1 mL of trioctylphosphine (2.2 mmol, 22 equiv.) and 3 mL of sodium naphthalenide (0.3 mmol, solution in THF, 0.1 mol/L) are added to 0.5 mL of $InCl_3$ (0.1 mmol, solution on THF, 0.2 mol/L, at room temperature). The solution turns immediately to brown.

Preparation of InP nanoparticles: The solution of In nanoparticles is used as synthesized. 0.43 mL of $P_4$ (0.1 mmol of P, 1 equiv. of P, solution in toluene, 0.23 mol/L of P) is added at room temperature. The resulting InP nanoparticles are isolated by washing and centrifugation with isopropanol.

For EDS characterization, the nanoparticles were synthesized using 1 mL of trioctylamine (TOA) (23 equiv.) instead of trioctylphosphine.

### 2.2 Synthesis of $Zn_3P_2$ nanoparticles

Preparation of Zn nanoparticles: 1.0 mL of trioctylphosphine (TOP, 2.2 mmol, 22 eq.) is added to 2.5 mL of THF in a Schlenk flask. 13.6 mg of $ZnCl_2$ (0.1 mmol) are added in the solution. 2mL of sodium naphthalenide (0.2 mmol, solution in THF, 0.1 mol/L). The solution turns immediately to brown.

Preparation of $Zn_3P_2$ nanoparticles: The solution of Zn nanoparticles is used as synthesized. 0.148 mL of $P_4$ (0.067 mmol of P, solution in toluene, 0.45 mol/L of P) is added at room temperature. The solution is heated at 60°C for 1h. The resulting $Zn_3P_2$ nanoparticles are isolated by washing and centrifugation with isopropanol.

For EDS characterization, the nanoparticles were synthesized using 1 mL of trioctylamine (23 equiv.) instead of trioctylphosphine.

### 2.3 Synthesis of $Pb_2P$ nanoparticles

Preparation of Pb nanoparticles: the synthesis was conducted according to Aubin H. et al., J. Phys. Chem. C., 2009, 113, 7120. Briefly, 1 mL of a stock solution of $Pb(oleate)_2$ (1 mmol) and $Pb(acetate)_2,3\ H_2O$ (0.38 g, 1 mmol) are added to 2 mL of trioctylphosphine (4.5 mmol) and 1.80 g of octadecanol (6.7 mmol). The mixture is degassed and heated at 270°C under inert atmosphere for 15 min. The solution turns to dark brown. The particles are isolated by washing and centrifugation with isopropanol.

Preparation of $Pb_2P$ nanoparticles: 0.36 mL of $P_4$ (0.18 mmol of P, solution in toluene, 0.45 mol/L of P) and oleylamine (1 mL, 3.0 mmol) are added to lead nanoparticles (75 mg, 0.36 mmol of Pb) at room temperature. Toluene is evaporated at 60°C under vacuum. The mixture is then heated at 150°C for 1h under inert atmosphere. The resulting $Pb_2P$ nanoparticles are isolated by washing and centrifugation with isopropanol.

### 2.4 Synthesis of 'large' In nanoparticles

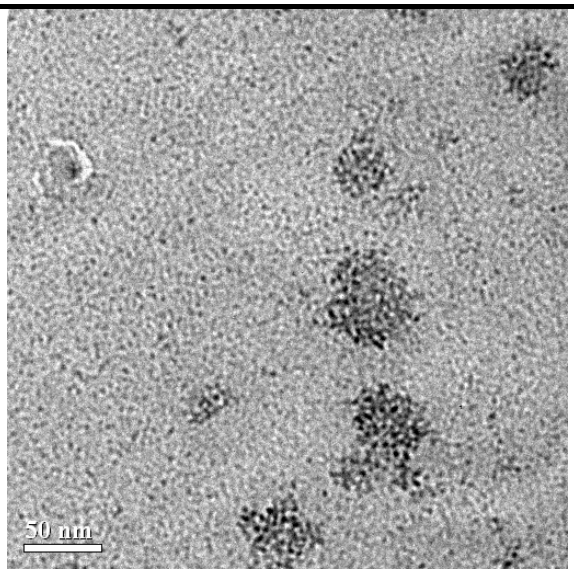
110.5 mg of $InCl_3$ (0.5 mmol, 1 equiv.) are dissolved in 25 mL of diethylene glycol (DEG). A solution containing 950 mg (25 mmol, 50 equiv.) of $NaBH_4$ dissolved in 25 mL of DEG and 1 mL of oleylamine (5 mmol, 10 equiv.) is swiftly added to the solution at room temperature under magnetic stirring. No change of color can be observed at this point. The solution is degazed and the flask is filled with $N_2$. The temperature is then raised to 100°C and kept for 2 hours. At this temperature, the solution turns from light yellow to dark brown within 5 minutes, indicating the formation of In(0) nanoparticles. The solution is cooled down to room temperature. The nanoparticles are isolated by centrifugation and washed with deionized water.

### 2.5 Synthesis of 'large' InP nanoparticles

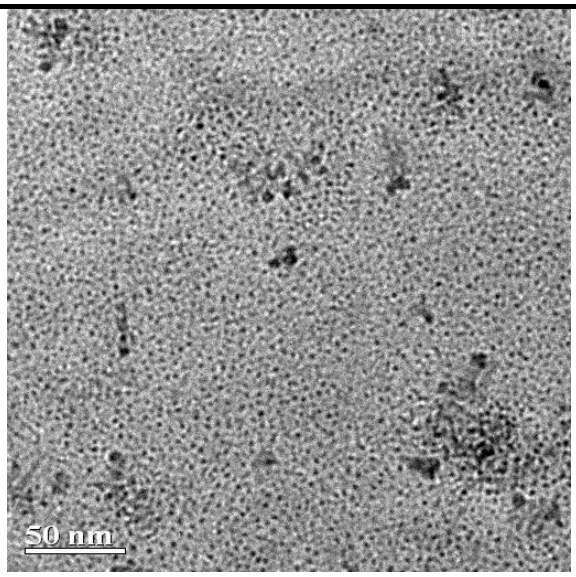
Indium nanoparticles (0.5 mmol of starting $InCl_3$, 1 equiv.) are dissolved in DEG (10 mL) under inert atmosphere. 1.08 mL of $P_4$ (0.125 mmol of P, solution in toluene, 0.46 mol/L of P,

1 equiv. of P) is added at room temperature. After evaporation of toluene under vacuum at 70°C, the solution is heated at 180°C for 2 hours. The resulting InP nanoparticles are isolated by centrifugation and washed with isopropanol.

**3. TEM observation for as-synthesized Zn nanoparticles**

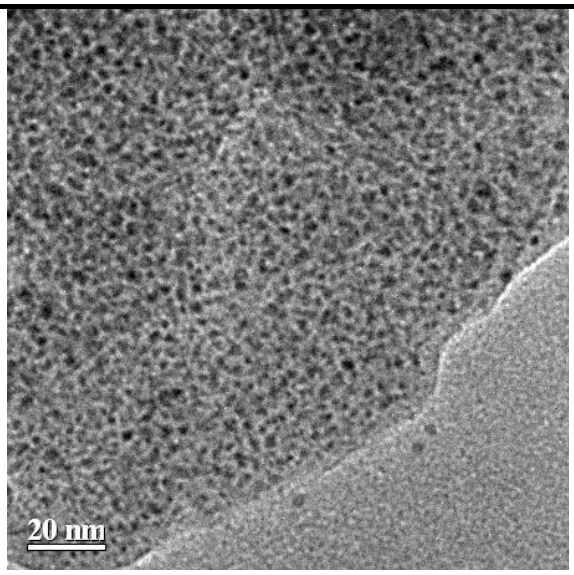



Zn NPs/TOP as-synthetised

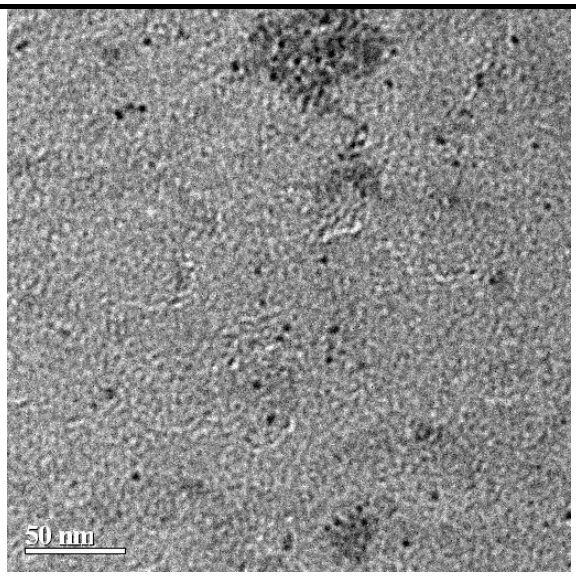



Zn NPs/TOA as-synthetised

**4. TEM observation for $Zn_3P_2$ nanoparticles**

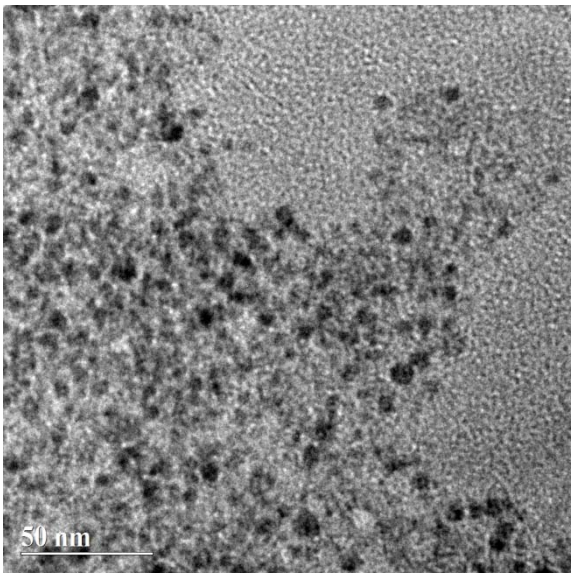



$Zn_3P_2$ nanoparticles/TOP (1-5 nm)

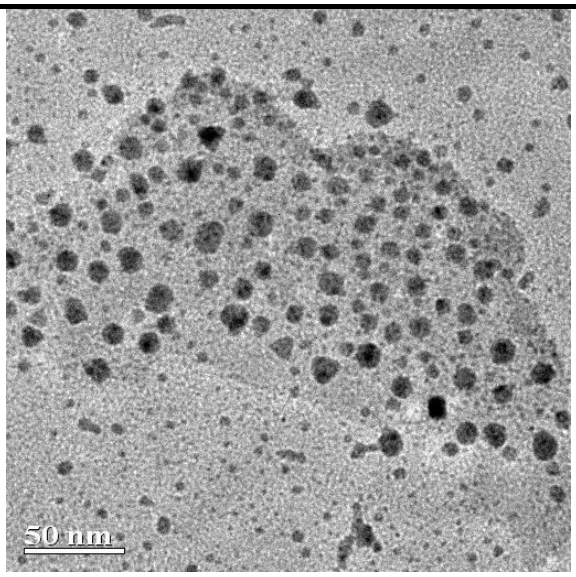



$Zn_3P_2$ nanoparticles/TOA (2-10 nm)

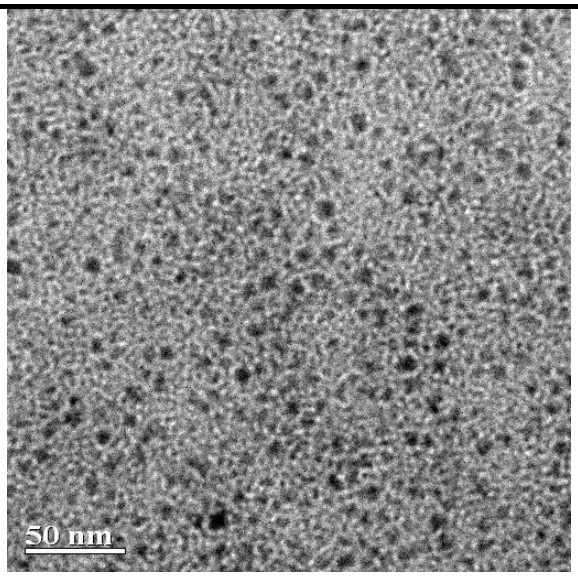
## 5. TEM observations of 'small' In nanoparticles synthesized with TOA for EDS analysis.




## 6. TEM observations of Pb nanoparticles and $Pb_2P$ nanoparticles.

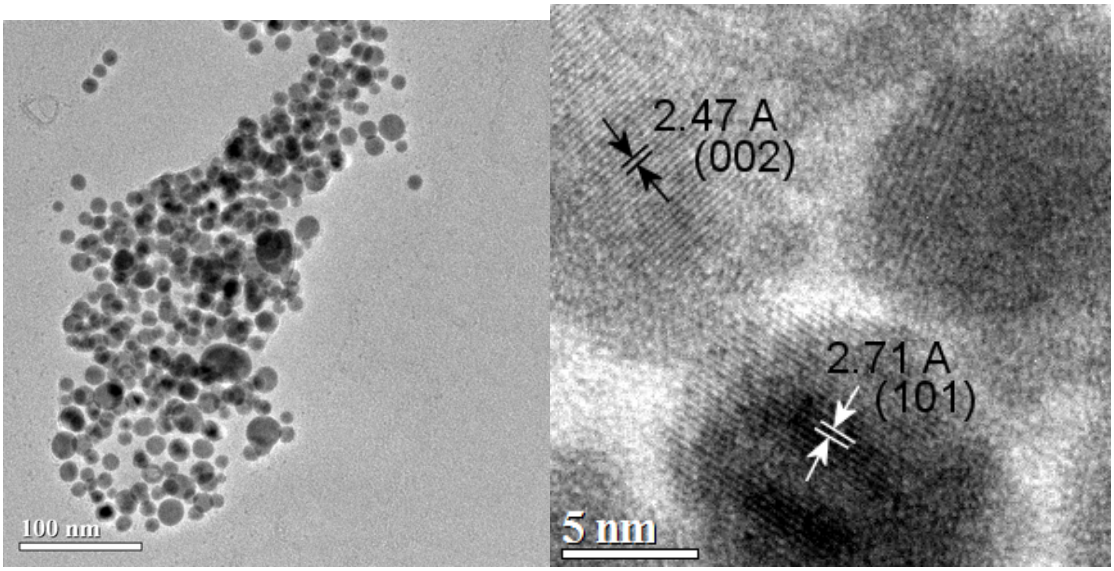



Pb nanoparticles (5-20 nm)

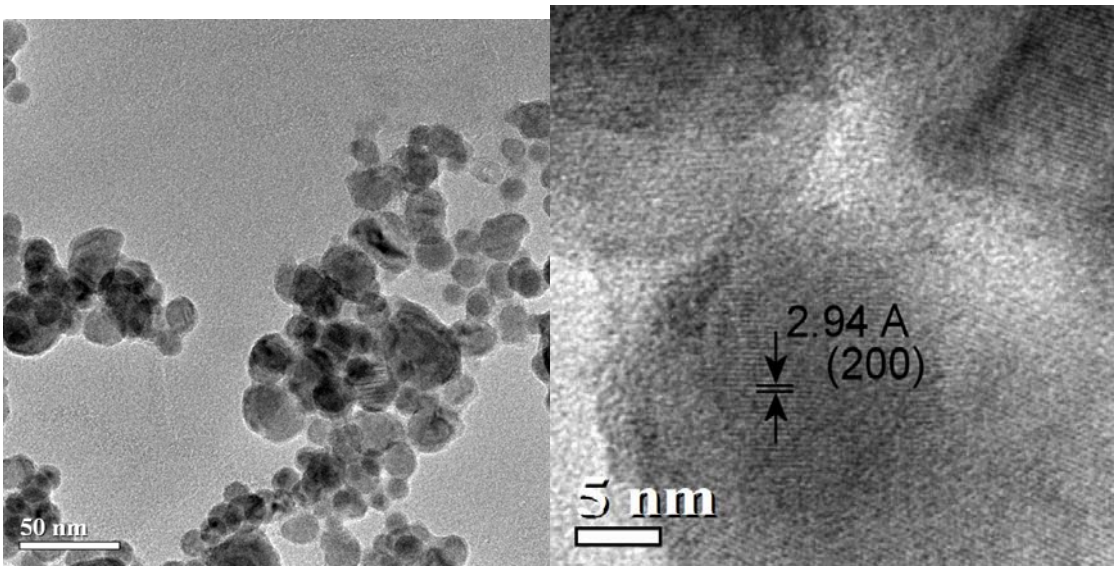



$Pb_2P$ nanoparticles (5-10 nm)

## 7. 'Large' In nanoparticles synthesized in DEG: TEM observations




## 8. 'Large' InP nanoparticles synthesized in DEG: TEM observations




[1] D.F. Shriver, *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley Interscience: New York, 1986.