Title: Phosphinecarboxamide based InZnP QDs - an air stable route to luminescent III-V semiconductors.

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Supporting information

Materials and methods

Indium chloride ($InCl_3$, 98%), zinc stearate (technical grade), hexadecylamine (HDA, 90%), zinc diethyldithiocarbamate (ZDEC, 97%) were purchased from Sigma-Aldrich and used as received. Phosphinecarboxamide was synthesized as previously described.[1] Hexane, ethanol, methanol, toluene and were purchased from Sigma-Aldrich and were used as received.
1-octadecene (1-ODE, technical grade, 90%) was purchased from Sigma-Aldrich and was degassed before use. 0.5M ZDEC stock solution was prepared in the glove box and filled with nitrogen while use.

Synthesis of InZnP core

To synthesize InZnP cores, 0.075g indium chloride ($InCl_3$, 3.4×10^{-4} mol), 0.43g zinc stearate ($Zn(COO(CH_2)_{15}CH_3)_2$, 6.8×10^{-4} mol), 0.105g phosphinecarboxamide ($PH_2C(O)NH_2$, 6.8×10^{-4} mol), 1.5g HDA (capping agent) and 20 mL 1-octadecene (1-ODE, solvent) ware added to a 100 mL three-necked flask in the glove box. The reaction system was degassed under vacuum with continuous stirring at 120 °C for either 30, 45 or 60 minutes, then backfilled with nitrogen, and heated up to 220 °C and reacted for 10 minutes, where the solution turned from clear red to clear saffron orange. Aliquots (5 mL) could be extracted with a degassed syringe.

Synthesis of InZnP/ZnS

The ZnS shell was deposited onto pre-prepared core particles by adding 0.3 mL of 0.1M ZDEC into reaction solution at room temperature, then heated at 300°C for 30 minutes under a nitrogen atmosphere, then cooled to room temperature.

Purification and re-dissolution of nanoparticles

The reaction solution, hexane and methanol in a volume ratio of 2:1:1 were mixed in a centrifuge tube (*ca*. 40 mL total), and the solution shaken for 30 seconds, then centrifuged for 3 minutes at 4000 rpm. The upper layer (hexane) which contained the nanoparticles was collected and added to an equal volume of methanol. The solution was shaken for 30 seconds, then centrifuged for 3 minutes at 4000 rpm. This was then repeated for one more time, then the upper layer (hexane) which contained the nanoparticles was collected. Methanol and ethanol (at a volume ratio of 7:3, 30 mL total) was added to the hexane solution (*ca.* 10 mL total), and the mixed solution was shaken for 30 seconds, then centrifuged for 5 minutes at 4500 rpm. The upper layers were removed, and the isolated particles were again redispersed in hexane (*ca.* 1-2 mL). Methanol and ethanol with volume ratio 8:2 (30 mL total) was added to the solution, the mixed solution was shaken for 30 seconds, and centrifuged for 5 minutes at 4500 rpm. This was then repeated, changing the methanol and ethanol volume ratio to 9:1 (30 mL total). The upper layer was removed, the nanoparticles were kept at the bottom of the centrifuge tube. The nanoparticles were dried overnight in the fume hood then re-dissolved in toluene and stored at room temperature in ambient conditions.

NMR Spectroscopy

NMR samples were prepared under the argon flow on a Schlenk-line in J-Young NMR tubes equipped with a gas-tight valve. NMR spectra were acquired on a Bruker AVIIIHD 400 MHz NMR spectrometer (^{31}P 162 MHz) and a Bruker AVIII 500 MHz NMR spectrometer (^{31}P 202 MHz). ^{31}P NMR spectra were externally referenced to 85% H_3PO_4 (δP 0 ppm).

Absorption and emission spectroscopy.

All spectra were measured in 1 cm path-length quartz cuvettes. UV-vis absorption spectroscopy was performed with a Hitachi U-4100 UV-vis-NIR spectrophotometer. Photoluminescence spectra of cleaned, air-exposed samples were taken with a Horiba FluoroMax4 and an OceanOptics QE Pro modular spectrometer with excitation of a 365 nm ThorLabs laser diode and a 415 nm bandpass filter.

Photoluminescence quantum yield measurements (PLQY).

PLQY of the solution in water and toluene was measured using integrating sphere by exciting the samples at 450 nm.

Electron microscopy and elemental analysis.

QDs in toluene were cleaned a further 3 to 5 times using the method described previously, diluted in toluene and drop-cast onto 3 nm ultra-thin holey carbon TEM grids from Agar Scientific. TEM images were taken on a JEOL JEM-2100 with a Gatan Orius CCD camera or a FEI Tecnai T20, both operating at 80 kV. Energy-dispersive X-ray spectra (EDS) were obtained with an Oxford Instruments 80 mm thin-window EDS detector (XEDX system) incorporated into the JEOL JEM-2100. STEM images were obtained with a FEI Titan G2 ChemiSTEM with accelerating voltage 200 kV and beam current 800 pA. EDS spectrum images were collected with the Titan's (SuperX) 4 SDD with total collection angle of 0.7 sr. The total spectrum image collection time was between 3 and 30 minutes with probe current of 40-180 pA. Energy-dispersive X-ray spectra (EDS) were also obtained with an Oxford Instruments 80 mm thin-window EDS detector with a 0.28 sr collection angle (XEDX system) incorporated into a JEOL JEM-2100. Elemental quantification was performed using a standardless Cliff Lorimer analysis.

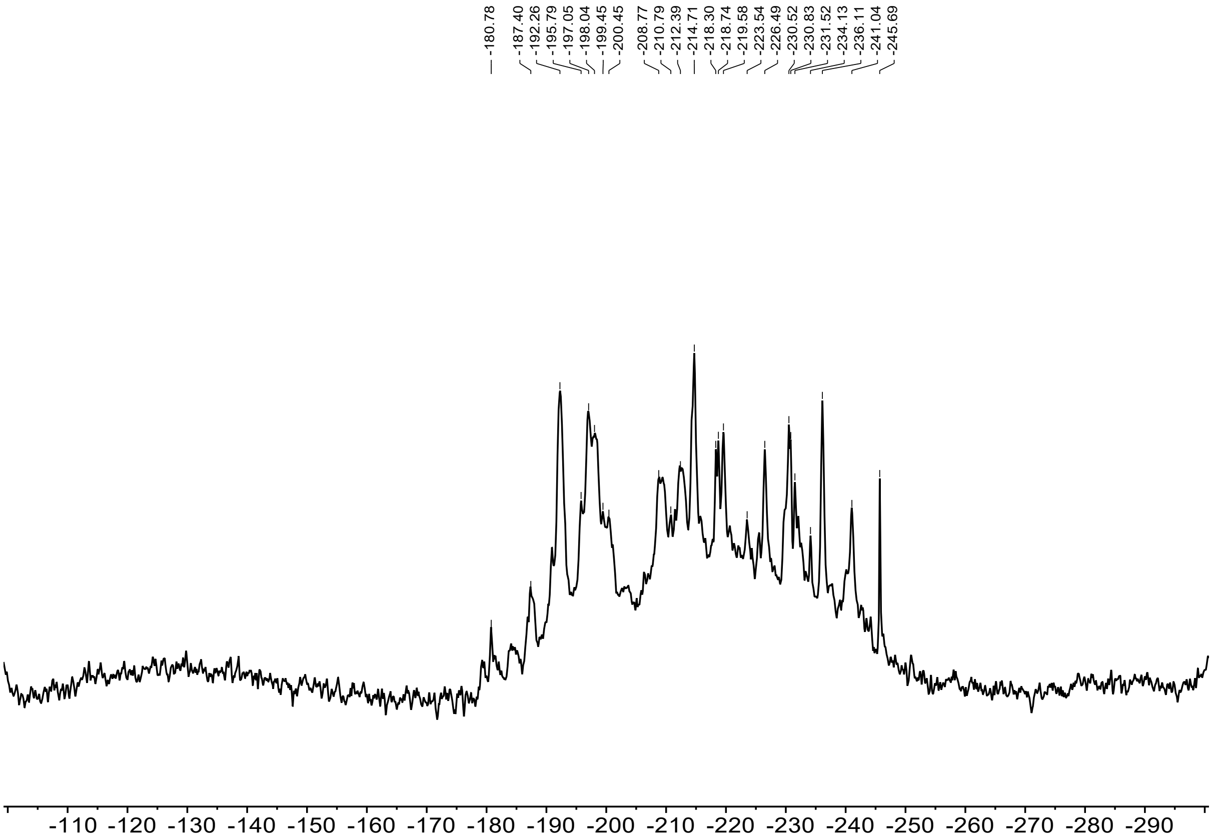
HAADF-STEM imaging

High angle annular dark field (HAADF) imaging was carried out on the JEOL ARM300CF aberration-corrected transmission electron microscope at Diamond Light Source (Didcot, UK). The microscope was operated at 300kV acceleration voltage in scanning transmission electron microscope (STEM) mode. The convergence semi-angle created by the 40 μm condenser lens aperture is 33.6 mrad. The HAADF detector collection semi-angle at 15 cm camera length is from 47.7 mrad to 220.6 mrad.

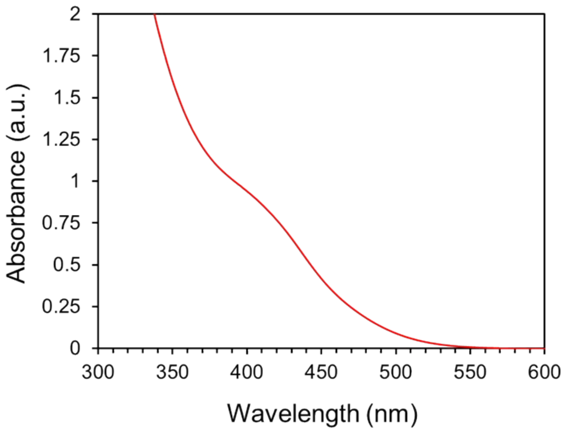
X-ray diffraction

Powder X-ray diffraction (XRD) was performed on a PANalytical X'Pert Pro diffractometer with a copper X-ray source at 1.5418 Å (50 kV, 40 mA). Data were collected in reflection geometry on a sample dropcast onto a silicon wafer placed on a spinning sample stage. The instrument was fitted with 0.04 rad. incident and receiving soller slits; an incident beam variable slit illuminating a 10 mm path; a 10 mm beam mask; incident and receiving antiscatter slits (1 deg. and 5 deg. respectively), and an X'Celerator detector preceded by a nickel filter.

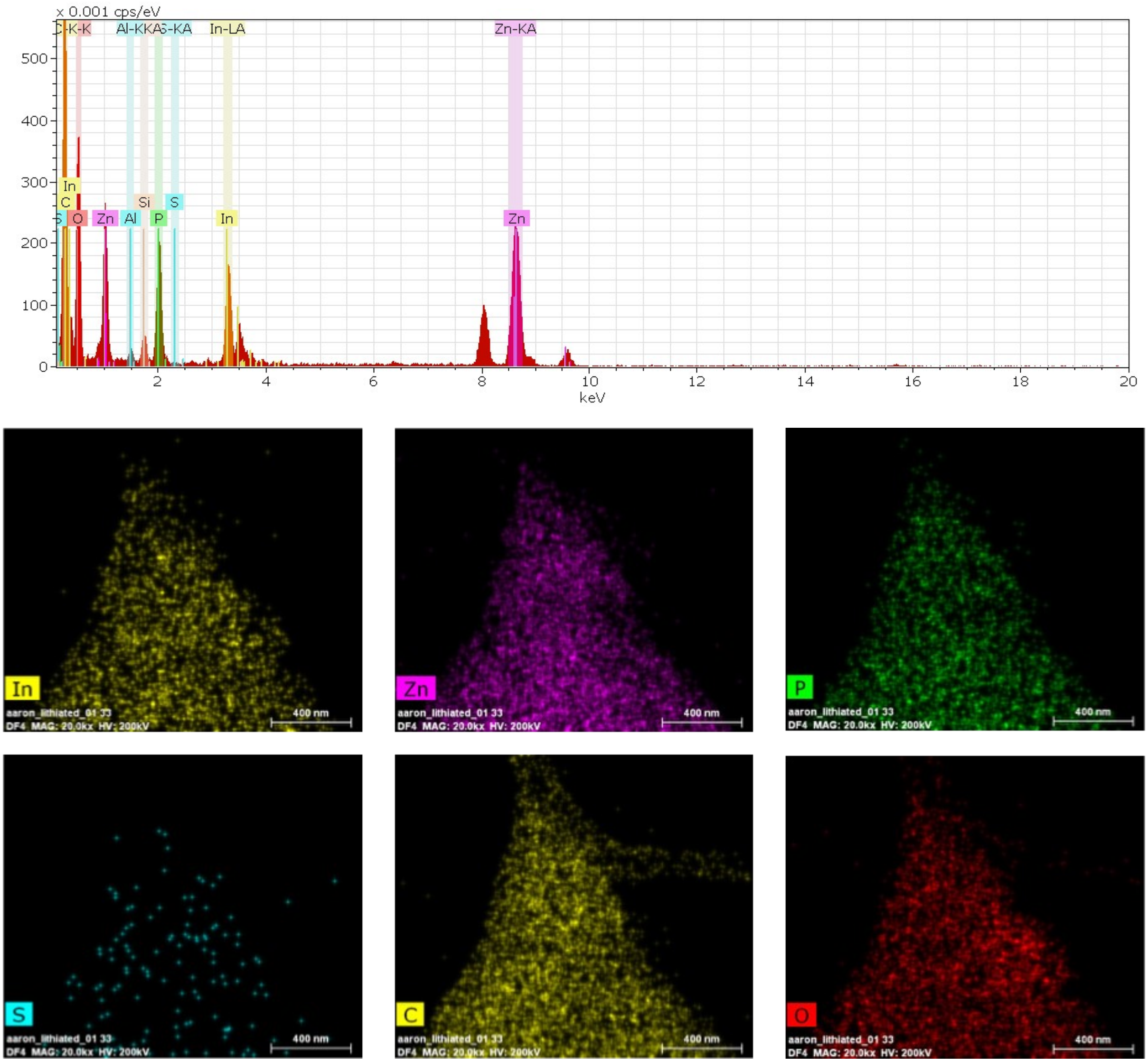
XRD reference patterns were obtained from the Inorganic Crystal Structure Database (ICSD). Zinc blende InP: ICSD-24517 (ICSD release 2023.1). Zinc blende ZnS: ICSD-230704 (ICSD release 2023.1)



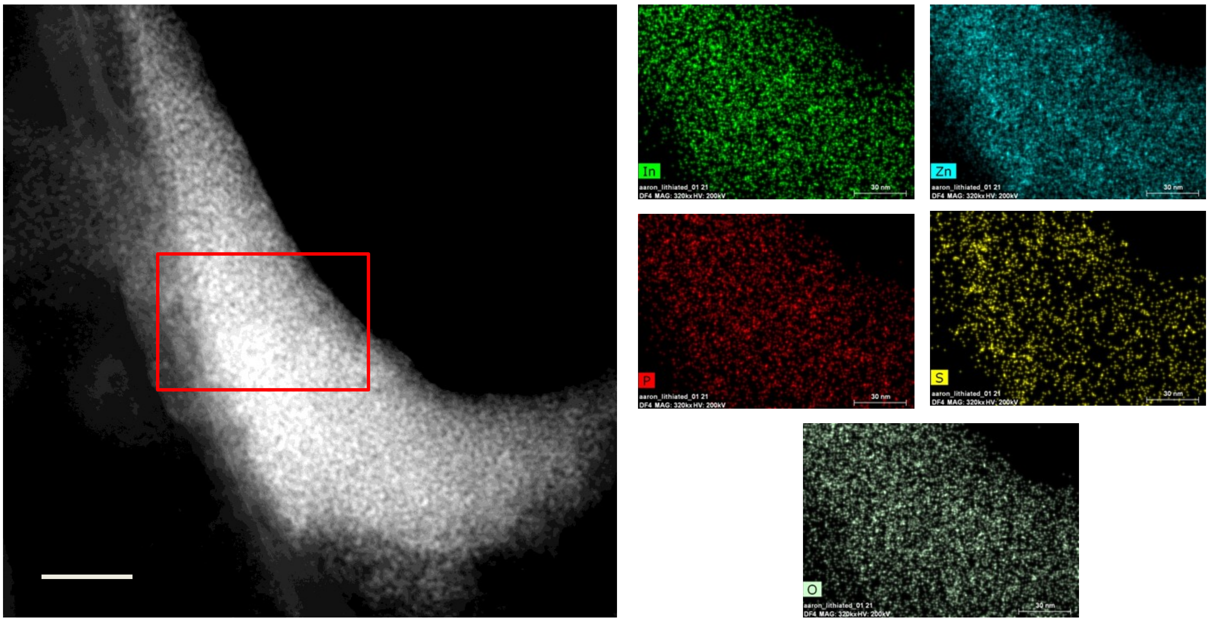
Supporting information figure 1: $^{31}P\{^{1}H\}$ NMR spectrum of product of the reaction between phosphinecarboxamide and indium phenylacetate at 110°C (THF- d_8).



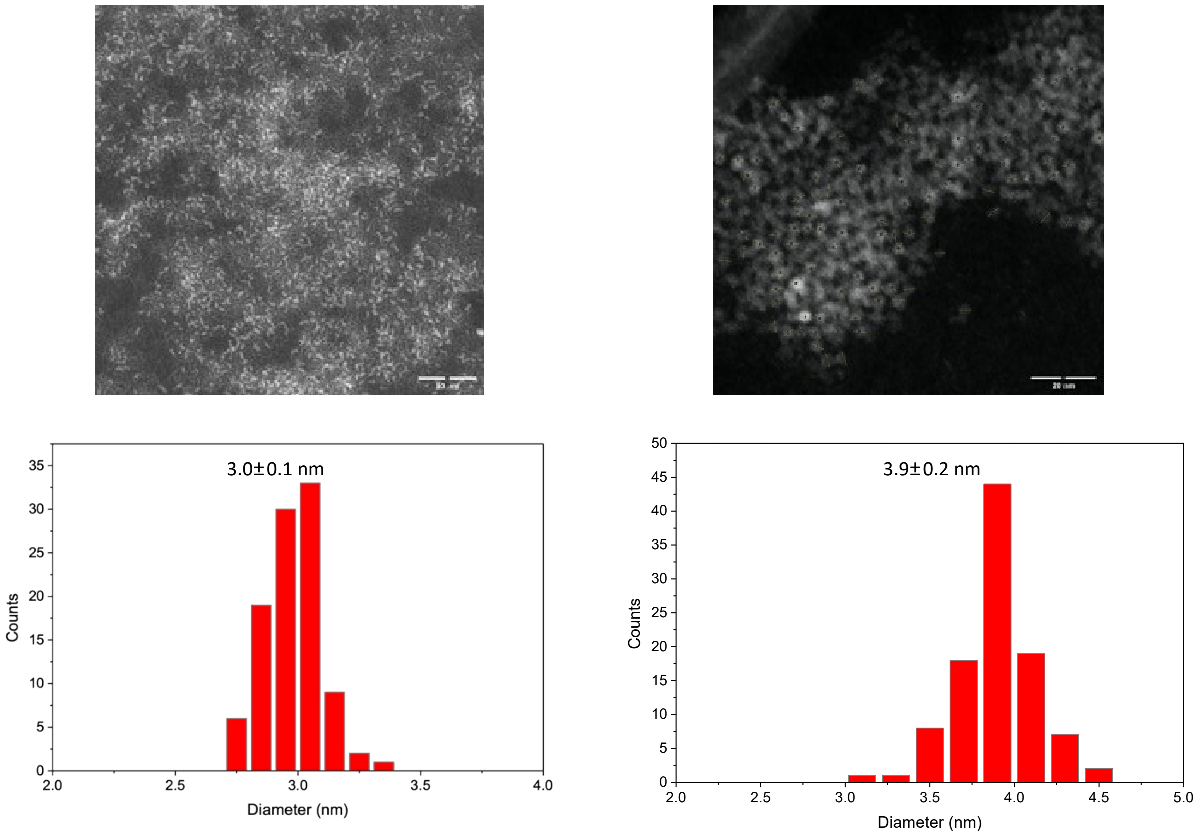
Supporting information figure 2**:** UV-Vis absorbance spectrum of InP cluster product.



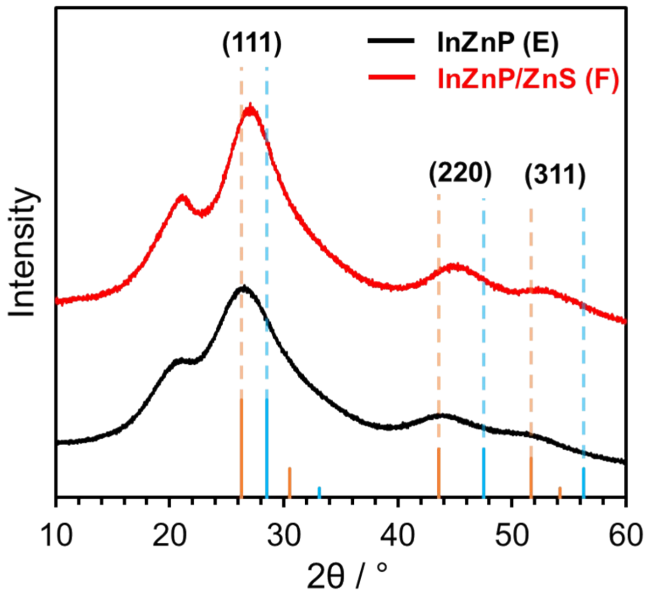
Supporting information figure 3: Elemental analysis of InZnP quantum dots (InZnP, grown at 45 minutes/120 °C followed by 10 minutes/220 °C) confirming the presence of elements consistent with the compound semiconductor, and a surface oxide species.



Supporting information figure 4: Electron microscopy and Elemental analysis for InZnP/ZnS particles (grown at 45 minutes/120 °C followed by 10 minutes/220 °C, followed by shell addition) scale bars = 30 nm.



Supporting information figure 5: Particle size distribution of InZnP (C), (left hand side) and InZnP/ZnS (D) (right hand side) QDs.



Supporting information figure 6: X-ray powder diffraction pattern and Miller indices of InZnP (E) and InZnP/ZnS (F) QDs. Bulk InP (orange trace) and bulk ZnS (blue trace) are shown for reference.

References

1 – Jupp, A. R.; Goicoechea, J. M. phosphinecarboxamide: a phosphorous-containing analogue of urea and stable primary phosphine. *J. Am. Chem. Soc*. **2013**, *135*, 19131 - 19134.