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Synthesis of NIR-emitting InAs-based core/shell quantum dots with the use of tripyrazolylarsane as arsenic precursor

Remo Tietze,^[a] René Panzer,^[b] Thorben Starzynski,^[a] Chris Guhrenz,^[a] Florian Frenzel,^[c] Christian Würth,^[c] Ute Resch-Genger,^[c] Jan J. Weigand,^{*[b]} and Alexander Eychmüller^{*[a]}

Remo Tietze, Thorben Starzynski, Chris Guhrenz, Prof. Dr. Alexander Eychmüller
Physical Chemistry, Technische Universität Dresden, Bergstraße 66b, 01062 Dresden,
Germany
E-mail: alexander.eychmueller@chemie.tu-dresden.de

Dr. René Panzer, Prof. Dr. Jan J. Weigand
Inorganic Molecular Chemistry, Technische Universität Dresden, Mommsenstraße 4, 01062
Dresden, Germany
E-mail: jan.weigand@tu-dresden.de

Florian Frenzel, Dr. Christian Würth, Dr. Ute Resch-Genger
Division Biophotonics, Federal Institute for Materials Research and Testing (BAM), Richard-
Willstaetter-Str.11, 12489 Berlin, Germany

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Abstract

Tris(3,5-dimethylpyrazolyl)arsane (**1**) is introduced as an low-cost and convenient to handle arsenic precursor for the straight forward synthesis of InAs quantum dots (QDs). Transamination of **1** with the solvent oleylamine (OLAH) gives trioylelarsane (As(OLA)₃) which in the presence of the reducing agents DIBAL-*H* or P(OLA)₃ yields InAs QDs *via* a typical hot injection approach. The size of the obtained InAs core QDs are tuned by varying the reaction time, the amount of the applied reducing agent, or even more effectively by changing the indium and/or zinc halide precursors, InX₃ and ZnX₂ (Cl, Br, or I). Passivation of the

resulting InAs particles with a protective ZnS or ZnSe shell results in improved photoluminescence (PL) of the core/shell QDs covering a spectral range between 600–1150 nm.

1. Introduction

In recent years group III-V semiconductor materials gained tremendous attention as less toxic surrogates for group II-VI nanomaterials in optoelectronic devices.^[1–6] Thereby, InAs QDs are one of the most promising candidates for near infrared (NIR) and short-wave IR applications, such as bio-imaging,^[7–9] photovoltaics,^[10,11] photodetectors,^[12,13] and lasers.^[14,15] Current synthetic approaches are challenging since hazardous As precursors, such as the highly pyrophoric and toxic tris(trimethylsilyl)arsane ($\text{As}(\text{SiMe}_3)_3$) is required. Those materials can only be handled under intense safety precautions, since they are often air and moisture sensitive and, in addition, in some cases commercially not available. Nevertheless, $\text{As}(\text{SiMe}_3)_3$ is the most commonly used arsenic precursor^[2,16] besides the less reactive $\text{As}(\text{GeMe}_3)_3$ ^[17] or highly toxic AsH_3 .^[18] Recently, SRIVASTAVA *et al.*^[19] and GRIGEL *et al.*^[20] highlighted tris(dimethylamino)arsane ($\text{As}(\text{NMe}_2)_3$) as commercially available precursor for the facile synthesis of InAs QDs. Mechanistically, $\text{As}(\text{NMe}_2)_3$ undergoes a transamination reaction with the solvent and reagent OLAH to give $\text{As}(\text{OLA})_3$ under the release of three equivalents of flammable dimethylamine. The reaction of $\text{As}(\text{OLA})_3$ with InCl_3 to InAs QDs does not proceed without the subsequent addition of a reducing agent for which typically DIBAL-*H*^[19] and nowadays also $\text{P}(\text{OLA})_3$ ^[20] or a *N,N*-dimethylethylamine complex (DMEA-AlH_3)^[21] are used. In the case of DIBAL-*H* and DMEA-AlH_3 , the As–N bonds are cleaved to give *in situ* $(\text{OLA})_x\text{AsH}_{3-x}$ species which react with the indium precursor to InAs QDs.^[22,23] With the applied concentration of DIBAL-*H* the size of InAs QDs can be tuned according to the method by SRIVASTAVA *et al.*^[19] In contrast, the approach by GRIGEL *et al.*^[20] applies *in situ* generated $\text{P}(\text{OLA})_3$ as reducing agent for the InAs QD synthesis (**Scheme 1**). This species is known to act both, as a remarkably efficient phosphorus precursor and reducing agent for the preparation of InP QDs.^[24,25,26] GRIGEL *et al.*^[20] pointed out that phase pure InAs QDs are obtained since

P(OLA)₃ only provides the electrons required for the reduction of As(OLA)₃ to InAs (**Scheme 1**).

In previous work we introduced tripyrazolylphosphanes (P(pyr)₃, *e.g.*, pyr = 3,5-dimethylpyrazole, **2**) for the convenient preparation of a long term stable (>6 months) P(OLA)₃ stock solution and its application for the synthesis of highly emitting InP/ZnS QDs.^[5,6] Derivatives of P(pyr)₃ are accessible on a multigram scale and represent a safe to handle, less toxic surrogate for cancerogenic hexaalkylphosphorous triamide derivatives such as P(NMe₂)₃ and P(NEt₂)₃. Moreover, the release of corrosive, flammable, and gaseous dialkylamines (Me₂NH, Et₂NH) during the transamination with OLAH is prevented. The released pyrazoles can easily be recovered in high yields (>94%) and reused for the precursor synthesis. The tripyrazolylarsane (As(pyr)₃, *e.g.*, pyr = 3,5-dimethylpyrazole, **1**) analogues are envisioned to react similarly, thus, representing a convenient to handle and stable arsenic precursor for the InAs QD synthesis.

The expansion of our previous results on P(pyr)₃ to the corresponding arsane derivative **1** for the synthesis of InAs QDs is topic of this contribution. For the initialization of the QD formation, DIBAL-*H* or P(OLA)₃ are used as reducing agents. In addition, the size of the resulting InAs particles are tuned by the used counter ions of the indium and zinc halides (Cl, Br, or I) and the reaction time, which has also a significant impact on the stability and luminescent properties. An additional enhancement is achieved by applying a protective zinc-containing (ZnSe, ZnS) passivating shell.

2. Results and Discussion

2.1. Preparation of a Pn(OLA)₃ (Pn = As or P) stock solution

Tripyrazolylpnictanes **1** and **2** are conveniently prepared *via* a modified procedure of FISCHER *et al.*^[27] by reacting the respective PnCl₃ (Pn = P, As) with trimethylsilylpyrazole derivative **3** (**Scheme 2**). The reactions are best performed under solvent free conditions and the products are obtained analytically pure in excellent yields (>98%) after removal of all volatiles. The

dissolution of **1** and **2** in OLAH yields stable Pn(OLA)_3 stock solutions from which the 3,5-dimethylpyrazole is recovered (>94%) by applying a vacuum treatment. The stock solution can be conveniently applied for the InAs QD synthesis by applying DIBAL-*H* or P(OLA)_3 as reducing agent.

2.2. Synthesis of InAs core QDs with different reducing agents

Reacting a 0.5 M As(OLA)_3 stock solution with the In precursor according to a typical InAs hot injection synthesis without adding a reducing agent does not lead to the expected color change which is an indication for the particle formation. In contrast, following the procedure of SRIVASTAVA *et al.*^[19] and GRIGEL *et al.*^[20] initializes particle formation and growth. The simultaneous injection of both the arsenic precursor and the reducing agent DIBAL-*H*^[19], yields InAs QDs. This is indicated by a color change of the reaction mixture to black (**Scheme 3**, synthetic route A (**SR A**)). In this approach, the addition of a Zn salt is not required. From spectroscopic investigations (**Figure S1**) the development of an excitonic feature at ~700 nm is observed after a growth time of 10 min. A shift up to ~950 nm is achieved with an increased reaction time of 30 min. A representative transmission electron microscopy (TEM) image of the resulting InAs particles is shown in **Figure 1a**. Additionally to the growth/reaction time, the amount of reducing agent plays an imperative role for tuning the InAs QD size (**Figure 1b**). For standard experiments in which the growth time was set to 15 min. and all other parameters kept constant, a decreased injection volume of DIBAL-*H* (200 μl , 1 M) shifts the first excitonic feature from ~750 nm to 1200 nm. Increasing the amount of DIBAL-*H*, however, leads to the formation of smaller QD sizes in accordance to observations by SRIVASTAVA *et al.*^[19], which is attributed to a faster nucleation caused by a higher concentration of As-H species. X-ray diffraction (XRD) measurements (**Figure 1c**) of the produced InAs QDs are in agreement with the cubic zinc blende crystal structure of bulk InAs (JCPDS-No. 15-896).

In the second synthetic approach, which requires the addition of a Zn salt, the stock solution of As(OLA)_3 prepared from **1** was directly applied (**Scheme 3**, synthetic route B (**SR B**)). For

comparison purpose, the synthetic parameters were kept almost identical for the InAs QD synthesis using either DIBAL-*H* (**SR A**) or P(OLA)₃ (**SR B**) as reducing agents. Typically, InCl₃ and ZnCl₂ are first dissolved in OLAH and heated under inert atmosphere to 190°C. After the addition of the As(OLA)₃ stock solution, three equivalents of P(OLA)₃ are injected leading to an immediate color change of the reaction mixtures to black indicating the formation of InAs core QDs. NMR spectroscopic monitoring of the reaction mixture proves the successive depletion of P(OLA)₃ ($\delta_{(31P)} = 97$ ppm) and the formation of the phosphonium salt [P(OLA)₄][Cl] ($\delta_{(31P)} = 29$ ppm; **Figure S2**). This is in agreement with the discussed redox reaction (**Scheme 1**) and the validation of QD formation by XRD investigations (**Figure S3**). The continuous red shift in the corresponding absorption spectra (**Figure 1d**) is in accordance with the growth of the InAs QDs. After 10 min and similar to **SR A**, the first excitonic transition is clearly present at ~725 nm which further shifts with time to ~1000 nm. The InAs QDs obtained according to **SR B** are phase pure and do not show any contamination with phosphorus, which was proven by ICP-OES measurements to determine the elemental composition (**Table S1**). Thus InCl₃ preferentially reacts with As(OLA)₃ to InAs.

Although zinc salts are not required for InAs following **SR A**, for **SR B** no QD formation is observed without the presence of zinc halides (ZnX₂, X = Cl, Br, or I) suggesting that a Lewis acid activation of the phosphorus based reducing agent P(OLA)₃ is required. Recent calculations by Laufersky *et al.*^[28] for the corresponding InP particles revealed that ZnCl₂ rapidly activates the phosphorus atom in P(OLA)₃, stabilizes energetically more favorable transition states, and promotes the formation of reduced In–P(I) species. As a consequence, a 5-fold excess of ZnX₂ was added in our QD synthesis according to **SR B** in order to overcome the activation barrier for the formation of the InAs QD. From other investigations^[25] it is known that the presence of In and/or Zn halides (InX₃, ZnX₂; X = Cl, Br, I) significantly influences the spectroscopic features by altering the size of the resulting particles. This observation is

discussed in terms of halide anion adsorption at the QD surfaces. The addition of modifiers such as carboxylic acids during the synthesis prevents this by the beneficial formation of $\text{In}(\text{carboxylate})_3$, $\text{Zn}(\text{carboxylate})_2$ and HX ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$). During our **SR B**, the formation of HX can be excluded since the solvent *OLAH* reacts as a base, thus, it can be anticipated that the present halides interact during the synthesis with the precursor and the QD surface. Similar assumptions have already been extensively studied for InP QDs using X-ray fluorescence spectroscopy (XRF).^[25] Based on these XRF measurements, the application of different indium and/or zinc halides should also directly influence the particle size growth and to the best of our knowledge this influence is now for the first time investigated on the synthesis for InAs QDs. Our **SR B** allows to investigate the influence, by the systematic change of the In and Zn metal halides InX_3 and ZnX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), on the size of the resulting InAs particles (**Figure 2**). While all other reaction parameters were kept the same (190°C injection and growth temperature, 15 min of growth time) the absorption is shifted from ~540 nm, to ~650 nm to ~820 nm for ZnI_2 , ZnBr_2 , and ZnCl_2 , respectively (**Figure 2a**). From TEM images shown in **Figure 3** we determined the average size of core InAs particles synthesized with ZnBr_2 and ZnCl_2 to 3.5 nm and 5.1 nm, respectively. This is the first literature report of a shift of the first excitonic transition of InAs QDs below 600 nm. Typically, the first transition is located between 650 nm and 750 nm if $\text{As}(\text{TMS})_3$ ^[27], AsH_3 ^[18] or $\text{As}(\text{NMe}_2)_3$ ^[20] are used as As precursors. Our investigations on the influence of the InX_3 precursor show a similar trend and absorption features at ~810 nm, ~720 nm, and ~650 nm are observed applying the corresponding metal halides InCl_3 , InBr_3 and InI_3 , respectively (**Figure 2b**). Based on these results, it can be concluded that the use of larger, i.e., more voluminous halide anions ($\text{I} > \text{Br} > \text{Cl}$) leads to a faster nucleation and, therefore, the formation of smaller InAs QDs similarly to the discussed effects elsewhere^[25] which is based on differences in the reaction rates as a result of the adsorption of the halide ions on the particle surface.

In comparison to our results and to Laifersky *et al*, it can be rationalized that with increasing atom number of the halides ($\text{Cl} > \text{Br} > \text{I}$) and the resulting reduced Lewis acidity of the ZnX_2 ($\text{ZnCl}_2 > \text{ZnBr}_2 > \text{ZnI}_2$), the strength of the electronic interaction in the presumed phosphorus–zinc halide complex is reduced which, consequently, speeds up the nucleation rate. For comparison, the results of both methods (**SR A** and **SR B**) are summarized in **Table 1**. Taking into account both reaction pathways, the QD size can be more easily tuned by the use of P(OLA)_3 as reducing agent. Not only a broader absorption region is covered applying **SR B** but also the particle size can be more effectively controlled by changing the zinc and/or indium halide precursor. Since both approaches provide non-emitting core QDs, the following section focuses on the enhancement of the stability and PL properties of the InAs QDs by coating with a protective ZnS or ZnSe shell. The initial InAs particles were produced *via* **SR B**.

2.3. Enhancement of the PL properties – shelling of InAs core QDs with ZnS(e)

In order to render the InAs QDs luminescent, a protecting ZnS or ZnSe shell was directly grown on the non-emissive InAs cores which were synthesized according to **SR B** and without further purification. A stepwise increase of the reaction temperature and an alternating addition of Zn(stearate)_2 dissolved in 1-octadecene with stoichiometric amounts of a tri-*n*-octylphosphine sulfide (TOP-S) or selenide (TOP-Se) precursor resulted in the formation of either InAs/ZnS or InAs/ZnSe core/shell QDs. **Figure S4** shows the corresponding absorption spectra of the initial InAs cores and the resulting InAs/ZnS QDs. A red shift of the first excitonic feature, which is distinctive for a type-I band alignment, indicates the successful growth of a ZnS shell. Another impressive evidence of the successful QD core passivation is the observed strong PL (**Figure S5**) with emission peaks at 937 nm and 1029 nm for InAs/ZnS and InAs/ZnSe QDs, respectively. The discrepancy of the emission maxima of ZnS- and ZnSe-shelled nanomaterials is caused by differences in the band alignment of the resulting type-I core/shell structure. The mean fluorescence lifetimes of the resulting core/shell particles shelled with ZnS and ZnSe are determined to be 62 ns and 49 ns (**Figure S6**). The photoluminescence quantum yields (PL

QYs) of both systems were determined to about 10% (InAs/ZnS) and about 8% (InAs/ZnSe). These values are comparable with the results obtained by GRIGEL *et al.*^[20] Additional XRD measurements (**Figure S7**) clearly indicate the formation of a passivating ZnS and ZnSe shell. Due to the high reaction temperatures an alloying process near the interface of the core and shell material shifts the (111) reflexes towards the pure zinc-containing shell material. This can be explained by a partial migration of zinc ions into the InAs core region, as it is also observed in the synthesis of InP/ZnS QDs.^[5,6] TEM measurements of the resulting spherical InAs/ZnS QDs exhibit an increase in the nanoparticle size compared to the original core particles and confirms additionally the growth of a ZnS protective layer (**Figure S4**). **SR B** results in a halide dependent InAs core size tuning, thus, subsequently, also the ZnS shelling of these QDs synthesized by using ZnBr₂ and ZnI₂ was investigated. The PL of the resulting InAs/ZnS QDs is shifted to shorter wavelengths applying ZnBr₂ (PL_{max} at 770 nm) instead of ZnCl₂ (PL_{max} at 900 nm) in accordance with a smaller core diameter (**Figure 4a**). However, attempts to obtain InAs/ZnS QDs using ZnI₂ did not proceed. This might be caused by etching of the small InAs core particles during the shelling process.

In contrast, ZnSe coating of both InAs QDs synthesized from ZnBr₂ and ZnI₂ following **SR B** was successful and the epitaxial shell growth shifts the emission towards 837 nm (ZnBr₂) and even 604 nm (ZnI₂; **Figure 4b**). Varying the initial InAs core size by changing the used ZnX₂ precursor provides PL control over a broad wavelength region ranging from 600 to 1050 nm and shifts the emission even into the visible range.

3. Conclusion

In summary, the application of tris(3,5-dimethylpyrazolyl)arsane (**1**) as efficient As precursor for the InAs QD synthesis is presented. **1** undergoes an *in situ* transamination with the solvent OLAH to yield a stable and easy to handle As(OLA)₃ stock solution. During its preparation, the 3,5-dimethylpyrazole can be removed with high yield (>94%) by a vacuum treatment and

reused in the synthesis of **1**. The resulting As(OLA)₃ solution is applied in the InAs QD synthesis in the presence of the reducing agents DIBAL-*H* and P(OLA)₃ to initialize the QD formation and growth. The resulting InAs core size can be conveniently tuned from the visible to the NIR wavelength region (~540 – 1200 nm) by varying the amount of DIBAL-*H* according to **SR A** or by changing the used metal halide (InX₃, ZnX₂ X= Cl, Br, I) by applying P(OLA)₃ (**SR B**). Shelling of the non-emissive InAs core particles with ZnS or ZnSe encourages photoluminescence (PL) and the resulting core/shell QDs cover a broad spectral region ranging from ~600 nm to ~1200 nm with comparable high PL QYs reaching values of up to 10 %.

4.1. Experimental Section

Chemicals

All chemicals used were of analytical grade or of the highest purity available. Indium chloride (Strem Chemicals, anhydrous, 99.99%), indium bromide (Sigma Aldrich, 99%), indium iodide (Sigma Aldrich, 99.998%), zinc chloride (Sigma Aldrich, anhydrous, 99.995%), zinc bromide (Grüssing, anhydrous, 99%), zinc iodide (Acros, anhydrous, 98%), zinc stearate (Sigma Aldrich, purum), oleylamine (OLAH, Sigma Aldrich, 70%), diisobutylaluminiumhydride (DIBAL-*H*, Sigma Aldrich, 1M solution in toluene), sulfur flakes (ABCR), selenium powder (Chempur, 160 mesh, 99.99%), toluene (Sigma Aldrich, p.A.), and ethanol (technical grade). AsCl₃, PCl₃, 3,5-dimethylpyrazole and Me₃SiCl were purchased from Sigma Aldrich. Dry, oxygen-free OLAH was distilled from CaH₂ and stored under nitrogen. Deuterated benzene (C₆D₆) was purchased from Sigma Aldrich and distilled from potassium. All glassware was oven-dried at 160°C prior to use. Tris(3,5-dimethylpyrazolyl)phosphane **2** and the 0.5 M P(OLA)₃ stock-solution was obtained according to literature procedures.^[5]

Precursor Preparation

Synthesis of tris(3,5-dimethyl)-1*H*-pyrazol-1-yl)arsane (**1**)

To a cooled solution (0°C) of 1-(trimethylsilyl)-3,5-dimethyl-1*H*-pyrazole (18.9 g, 0.11 mol) a solution of AsCl₃ (0.57 mL, 6.81 mmol) is added dropwise. The reaction mixture is stirred at room temperature for 16 h and the colorless solid product **2** (9.88 g, 98%) is obtained after the removal of all volatiles under vacuum.

Mp.: 105–109°C; **IR** (KBr, 300 K, [cm⁻¹]): ν = 3202(vw), 3131(vw), 3110(vw), 3038(vw), 2976(vw), 2959(vw), 2931(m), 1561(vw), 1551(m), 1439(w), 1408(m), 1319(vw), 1295(vs), 1246(vw), 1152(w), 1109(m), 1018(w), 964(m), 801(w), 786(s), 754(w), 738(w), 587(w), 470(m), 461(w); **¹H NMR** (CD₂Cl₂, 300 K, [ppm]): δ = 2.02 (9H, s, C5–H), 2.21 (9H, s, C1–

H), 5.97 (3H, m, C3–H); ^{13}C NMR (CD_2Cl_2 , 300 K, [ppm]): δ = 11.3 (3C, s, C5), 13.8 (3C, s, C1), 108.9 (s, 3C, C3), 147.5 (3C, s, C4), 152.9 (3C, s, C2); m/z (EI): 42(4), 81(5), 91(4), 95(28), 96(64), 97(8), 169(6), 170(20), 171(4), 264(6), 266(100), 267(12), 289(7), 360(3), 396(25). Elemental analysis: calc. for $\text{C}_{15}\text{H}_{21}\text{AsN}_6$: 23.3 N, 50.0 C, 5.9 H found: 23.2 N, 50.2 C, 5.9 H.

InAs core QD synthesis

Synthesis of InAs core QDs with DIBAL-H – synthetic route A (SR A)

The InAs QD synthesis was performed with slight variations according to SRIVASTAVA *et al.*^[19] In a standard approach 0.2 mmol of InCl_3 (44.24 mg) and 5 mL of OLAH are loaded in a 25 mL three-necked flask and vacuum was applied for 30 min at 120°C. Under nitrogen atmosphere the temperature was increased to 250°C. Simultaneously 0.4 mL (0.2 mmol) of a 0.5 M solution of As(OLA)_3 and 1.2 mL of 1 M DIBAL-*H* in toluene (variation between 0.2 mL and 1.2 mL leads to different QD sizes) were injected rapidly into the reaction flask which results in a colored, i.e., black crude solution. The QDs were typically allowed to grow at 250°C for 5–30 min. Afterwards the reaction mixture was cooled to room temperature and diluted with 10 mL of toluene. 15 mL of ethanol were added to the crude solution to precipitate the QDs by centrifugation. The precipitated QDs were redispersed in toluene or TCE and centrifuged again to remove by-products of the InAs core synthesis. Following, the colloidal QD solution was additionally washed with ethanol and finally redispersed in toluene.

Synthesis of InAs core QDs with P(OLA)_3 – synthetic route B (SR B)

The procedure follows with slight variations GRIGEL *et al.*^[20] In a standard synthesis 0.2 mmol (44.24 mg) of InCl_3 , 4.4 mmol of Zn(X)_2 ($\text{X} = \text{Cl, Br, or I}$), and 5 mL of OLAH were loaded in a 25 mL three-necked flask and vacuum was applied for 30 min at 120°C. Following, the temperature was raised under inert atmosphere to 190°C and 0.2 mmol (0.4 mL) of a 0.5 M

solution of As(OLA)_3 was injected into the reaction mixture. After 1 min of stirring 1.2 mL (0.6 mmol) of a 0.5 M solution of P(OLA)_3 was quickly injected to initialize the QD formation. The QDs were typically allowed to grow at 190°C for 15 min. Afterwards the reaction mixture was cooled down to room temperature and diluted with 15 mL of ethanol to precipitate the QDs. The precipitated particles were redispersed in toluene and centrifuged again to separate from byproducts. The colloidal QD solution was cleaned once more by precipitation and dissolution using ethanol and toluene as non-solvent and solvent, respectively.

ZnS(e) shelling procedure

ZnS shelling of InAs core QDs

Typically the synthesis of InAs core QDs applying SR B is carried out for 15 min at 190°C . For growing a ZnS shell the crude solution is kept at the reaction temperature and 1 mL of stoichiometric TOP-S (2.2 M) is slowly injected. After 60 min the temperature is increased from 190°C to 200°C . At 120 min 1 g of Zn(stearate)_2 in 6 mL of ODE are slowly injected and the temperature is raised from 200°C to 220°C . After 150 min 0.7 mL of TOP-S (2.2 M) are injected and the reaction temperature is increased from 220°C to 240°C . To increase the shell thickness 0.5 g of Zn(stearate)_2 in 3 mL of ODE are slowly added after 180 min and the temperature is raised from 240°C to 260°C . Finally, the synthesis of InAs/ZnS core/shell QDs is quenched after 210 min and washed by precipitation with ethanol. The purified QDs are suspended in toluene. This procedure follows with slight variations GRIGEL *et al.*^[20]

ZnSe shelling of InAs core QDs

Typically, InAs core QDs were grown for 15 min at 190°C applying SR B. Following, the resulting InAs core QDs were shelled with slight variations according to GRIGEL *et al.*^[20] The crude solution is kept at the initial reaction temperature of 190°C and 1 mL of stoichiometric TOP-Se (2.2 M) is slowly injected. After stirring for 60 min the temperature is increased from

190°C to 200°C. At 120 min 1 g of Zn(stearate)₂ in 6 mL of ODE are slowly injected and the temperature is raised from 200°C to 220°C. 150 min after starting the shell growth 0.7 mL of TOP-Se (2.2 M) are injected and the reaction temperature is increased from 220°C to 240°C. Finally, 0.5 g of Zn(stearate)₂ in 3 mL of ODE are slowly added after 180 min to increase the shell thickness and the temperature is additionally raised from 240°C to 260°C. The synthesis of InAs/ZnSe QDs is quenched after 210 min shelling time and the crude solution is washed by using ethanol and toluene as non-solvent and solvent, respectively.

Purification procedure of core/shell QDs

To purify the core/shell QDs from byproducts, 15 mL of ethanol are added to the reaction mixture and centrifuged at 4500 rpm for 5 min. The supernatant is discarded and the precipitate is suspended in 4 mL of toluene or TCE depending on further processing. The QDs are redispersed by the use of ultrasonication and centrifuged at 3000 rpm for 3 min. The resulting supernatant is used for further characterization and processing.

Characterization techniques

Nuclear magnetic resonance (NMR) spectra were measured on a Bruker AVANCE III HD Nanobay (¹H (400.13 MHz), ¹³C (100.61 MHz), ³¹P (161.98 MHz)), on a 400 MHz UltraSield, or on a Bruker AVANCE III HDX, 500 MHz Ascend (¹H (500.13 MHz), ¹³C (125.75 MHz), ³¹P (202.45 MHz)). All ¹³C NMR spectra were exclusively recorded with composite pulse decoupling. Chemical shifts (δ) were referenced to δ_{TMS} = 0.00 ppm (¹H, ¹³C) and δ_{H3PO4(85%)} = 0.00 ppm (³¹P, externally) and are reported in ppm. Coupling constants (J) are reported in Hz.

Absolute PL QY measurements were performed with a calibrated integrating sphere setup equipped with a 450 W xenon lamp, coupled to a single monochromator as excitation channel. For QY determination, the luminescence intensity of dispersed InAs QDs was measured in the spectral range of 800 – 1150 nm using two detectors, a Si-CCD and an InGaAs-CCD, spectrally

corrected, and subsequently integrated.^[30,31] The measurements were performed using 10x4 mm quartz cuvettes. The values of the absorbances of the dispersed InAs QDs at the excitation wavelength of 750 nm were between 0.08 and 0.1.

UV/Vis absorption spectra of the QD solutions were recorded using a Cary 50 and Cary 5000 spectrophotometer (Varian).

PL spectra were measured on a FluoroLog-3 spectrofluorometer (Horiba Jobin Yvon Inc.) using variable excitation wavelength of 450 to 700 nm depending on the nature of the sample. The samples were prepared by dispersing the NCs in toluene or TCE depending on their spectroscopic features.

PL lifetimes were measured using a FluoroLog-3 spectrofluorometer (Horiba Jobin Yvon) equipped with a pulsed laser diode (410 nm) and a TCSPC module at room temperature. Average PL lifetimes were calculated at the time, where the initial signal intensity was reduced to 1000 counts/e.

Powder X-ray diffraction (XRD) patterns were collected in reflection mode with a Bruker AXS D2 PHASER diffraction system using Cu K- α irradiation ($\lambda = 1.5406 \text{ \AA}$) and a LYNXEYE/SSD160 detector.

Inductively coupled plasma–optical emission spectroscopy (ICP-OES) measurements were carried out on a Perkin-Elmer Optima 7000DV optical emission spectrometer. All calibration standard solutions were matrix matched. Concentrated aqua regia and deionized water were used to prepare the analyzing solutions.

Transmission electron microscopy (TEM) of the QDs was performed using a FEI Tecnai F30 microscope operated at 300 kV and JEOL JEM-1400Plus microscope operated at 120 kV.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Scheme 1. Proposed redox reaction for the formation of InAs QDs applying P(OLA)_3 as reducing agent.^[20] As(OLA)_3 and P(OLA)_3 are formed in situ from the corresponding $\text{Pn(NMe}_2)_3$ ($\text{Pn} = \text{As}$ or P) precursors via transamination with OLAH .

Scheme 2. Tris(3,5-dimethylpyrazolyl)arsane (**1**) and tris(3,5-dimethylpyrazolyl)phosphane (**2**) are synthesized via the reaction of trimethylsilylpyrazole (**3**) with PnCl_3 ($\text{Pn} = \text{As}$, P), respectively; i) neat, 16 h, room temperature. Dissolution of **1** and **2** in OLAH yields under recovery of the pyrazole stable Pn(OLA)_3 stock solutions.

Scheme 3. Different synthetic approaches applied for the InAs QD formation using the previously prepared As(OLA)_3 stock solution. Following **SR A**, DIBAL-H is added as the reducing agent yielding InAs QDs. Applying **SR B** a zinc activation of the reducing agent P(OLA)_3 is necessary to promote the formation of InAs QDs.

Figure 1. (a) Representative TEM image of InAs QDs synthesized with DIBAL-*H* as reducing agent (SR A). (b) Shift of the absorption by varying the amount of reducing agent (DIBAL-*H*) used for the InAs QD synthesis and (c) confirmation of the cubic zinc blend structure (JCPDS-No. 15-896) of the resulting InAs QDs by XRD measurements. (d) Evolution of the excitonic absorption feature of the InAs QD synthesis with progressing reaction time applying P(OLA)₃ as reducing agent (SR B).

Figure 2. Variation of the used ZnX_2 (a) and InX_3 (b) for the InAs QD synthesis applying **SR B** ($\text{X} = \text{Cl, Br, I}$); The observed blue shift in the absorption spectra correlates with an increase of the halide atomic number; the reaction time was set to 15 min and the injection and growth temperature to 190°C; the concentration of ZnX_2 (a) and InX_3 (b) were kept constant.

Figure 3. Representative TEM images of differently sized core InAs particles following **SR B** by the use of ZnBr_2 (a) and ZnCl_2 (b). The average size of the QDs has been determined to 3.5 nm (a) and 5.1 nm (b).

Table 1. Comparison of the absorption features applying both DIBAL-*H* (**SR A**) and P(OLA)₃ (**SR B**) as reducing agents for the InAs QD synthesis.

Synthetic Route	SR A		SR B	
	-	ZnI ₂	ZnBr ₂	ZnCl ₂
Absorption	750 – 1200 nm	540 – 620 nm	610 – 715 nm	700 – 1000 nm

Figure 4. (a) Absorption and PL spectra of the resulting InAs/ZnS core/shell QDs applying SR B and InCl₃ and different ZnX₂ precursors for the core synthesis. (b) Absorption and PL spectra of the resulting InAs/ZnSe core/shell QDs applying SR B and InCl₃ and different ZnX₂ precursors for the core synthesis. Due to a faster nucleation rate the spectra are blue-shifted with increasing atomic number. This shows the influence of the used zinc halide on the initial InAs core size and, in consequence, on the PL of the final core/shell structure.

Table of contents entry:

Core/shell InAs/ZnS(e) quantum dots covering a broad spectral region in the visible and near infrared (600–1050 nm) and reaching photoluminescence quantum yields of up to 10% were synthesized *via* two different reaction pathways using a tripyrazolylarsanes. The applied reducing reagent DIBAL-*H* or P(OLA)₃ in combination with different metal halides (InX₃, ZnX₂, X = Cl, Br, or I) allows an efficient tuning of the initial InAs core size and their photophysical properties.

Keyword: InAs, [As] precursor, quantum dots, waste prevention, emission tuning

Remo Tietze, René Panzer, Thorben Starzynski, Chris Guhrenz, Florian Frenzel, Christian Würth, Ute Resch-Genger, Jan J. Weigand and Alexander Eychmüller

Synthesis of NIR-emitting InAs-based core/shell quantum dots with the use of tripyrazolylarsane as arsenic precursor