A developed Ullmann reaction to III–V semiconductor nanocrystals in sealed vacuum tubes†

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Group III–V (13–15, III = Ga, In, and V = P, As) semiconductor nanocrystals were effectively obtained *via* a developed Ullmann reaction route through the reactions of preformed nanoscale metallic indium or commercial gallium with triphenylphosphine (PPh₃) and triphenylarsine (AsPh₃) in sealed vacuum quartz tubes under moderate conditions at 320–400 °C for 8–24 h. The developed synthetic strategy in sealed vacuum tubes extends the synthesis of III–V semiconductor materials, and the air-stable PPh₃ and AsPh₃ with low toxicity provide good alternative pnicogen precursors for the synthesis of III–V nanocrystals. The analysis of XRD, ED and HRTEM established the production of one-dimensional (1D) metastable wurtzite (W) InP, InAs and GaP nanostructures in the zinc blende (ZB) products. Further investigations showed that 1D W nanostructures resulted from kinetic effects under the moderate synthesis of III–V nanocrystals was in the orders of IIIP > IIIAs and GaV > InV on the basis of experiments and thermodynamic calculations. Meanwhile, the microstructures and growth mechanism of the III–V nanocrystals were investigated.

Introduction

Group III-V (13-15) compounds are important semiconductors with high electron mobilities and larger exciton diameters, which make them widely-studied in electronic and optoelectronic devices,¹⁻³ high-speed electronics,^{4,5} and quantum size effects.⁶⁻¹² Chemical synthesis of III-V semiconductor materials and recently those within the nanometer scale can be carried out in solid,13,14 vapor¹⁵⁻²⁰ or liquid phase, or in solution^{6-12,21-29} as well as their hybrids.13-30 Many kinds of chemical reactions, such as elemental reactions,^{13,23-25} metathesis reactions,^{14,21,22} organometallic compound decomposition,^{6-12,18-20,26-30} and others^{15-17,31} are often involved in their synthesis, and all of them can efficiently lead to III-V semiconductor materials. However, the synthesis of III-V semiconductors of high quality still meets many problems, despite that there have been considerable efforts on the synthesis of III-V semiconductors in recent years. Synthetic reactions in the solid state must be conducted at high temperature, while organometallic compounds are usually highly toxic and unstable in air, which leads to complex synthesis procedures. Moreover, the higher covalent nature and less-available precursors also arouse many difficulties in the synthesis of III-V materials. Therefore, it is of much importance to seek novel pnicogen (N, P, As, Sb) sources and develop facile synthetic methods for III-V semiconductors from the perspective of chemistry and materials.

Triphenylphosphine (PPh_3) and triphenylarsine (AsPh₃) are widely used in organic synthesis and coordination chemistry

as common organic compounds containing VA elements, and they can serve as the effective precursors of P and As sources to synthesize III-V semiconductor nanocrystals. Meanwhile, the use of low-toxicity and air-stable PPh₃ and AsPh₃ as alternative pnicogen precursors can effectively avoid the employment of EH_3 , $(Na/K)_3E$, ECl_3 (E = P, As), P_4 , As or organometallic compounds of pnicogens such as tris(trimethylsilyl) phosphine [P(TMS)₃],^{6,8-10,12,29} tris(trimethylsilyl) arsine [As(TMS)₃]^{11,27} and trioctyl phosphine (TOP)³² with poor stability and high toxicity in the synthesis of III-V nanocrystals. The specific configurations of PPh₃ and AsPh₃ with high steric effects may induce some exceptional structures and shapes for III-V nanocrystals. On the basis of these ideas, we have successfully obtained InP and GaP nanocrystals from commercial bulk metal indium and gallium directly reacting with PPh₃.³³ Very recently, we have also synthesized InP and InAs nanocrystals through the reduction of metal chlorides with the above two triphenylpnictines in the presence of KBH₄ or Zn in benzene solution via a solvothermal process.³⁴ To extend the work^{33,34} in depth, here we report a developed Ullmann reaction route to III-V semiconductor nanocrystals in sealed vacuum quartz tubes at 320–400 °C for 8–24 h through the reactions of initial preformed metallic indium nanoparticles or commercial gallium with PPh₃ or AsPh₃. The reactions involved in the synthesis can be simplified as follows:

$$\mathbf{2III} + 2\text{VPh}_3 \xrightarrow{320-400 \text{ °C}} \mathbf{2IIIV} + 3\text{Ph} - \text{Ph}$$
(1)

where III = In, Ga, and V = P, As. Based on the above reactions, namely developed Ullmann reactions, we have successfully synthesized InP, InAs, GaP and GaAs nanocrystals. The designed synthetic strategy is facile and versatile, and it has been proven to be a good alternative route to III–V semiconductors and relevant compounds.

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Interestingly, investigations indicated that metastable wurtzite (W) InP, InAs and GaP were present in the as-synthesized onedimensional (1D) nanostructures (nanowires or nanorods) besides the main zinc blende (ZB) phase. Further investigations suggested that the moderately synthetic conditions (at 320–400 °C in sealed vacuum quartz tubes) and the employment of PPh₃ and AsPh₃ were favorable for the growth of W structured III–V nanocrystals. Moreover, the tendency for the synthesis of III–V nanocrystals could be arranged in the following order: IIIP > IIIAs and GaV > InV (III = Ga, In, and V = P, As) on the basis of experiments and thermodynamic calculations. In addition, investigation also suggested that the formation of the 1D III–V semiconductor nanostructures was attributable to the solution–liquid–solid (SLS) growth mechanism.^{6,26–29,35–38}

Experimental

Synthesis of III-V semiconductor nanocrystals

All materials were used as received without further purification. In a typical synthesis of InP nanocrystals, the mixture of 0.114 g newly-prepared indium nanocrystals³⁹ and 0.320 g PPh₃, of which the molar ratio of indium to PPh₃ was 1 : 1.2, was added into a quartz ampullaceous tube ($\phi 8 \text{ mm} \times 12 \text{ cm}$), which was then evacuated and sealed. The tube was horizontally kept in a resistance furnace at 400 °C for 8 h. The temperature increased from room temperature to 400 °C in 80 min. After the tube was naturally cooled to room temperature, the black products were collected, washed with benzene, diluted hydrochloric acid and absolute alcohol, and finally dried for further investigation.

As for the synthesis of InAs, GaP and GaAs nanocrystals, similar synthesis procedures were employed by changing corresponding reaction precursors with various molar ratios. The details of the conditions for the synthesis of III–V semiconductor nanocrystals were summarized in Table 1.

Characterization

The phase purity and crystallizability of the as-prepared products were determined by powder X-ray diffraction (XRD) using a Philips X'Pert Pro Super diffractometer with graphitemonochromatized Cu K α radiation ($\lambda = 1.54178$ Å). Morphologies and microstructures of the samples were examined by transmission electron microscopy (TEM, Hitachi model H-800), selected area electron diffraction (SAED) patterns, and highresolution TEM (HRTEM, JEOL-2010, used with an accelerating voltage of 200 kV). Energy-dispersive X-ray spectroscopy (EDX) images were recorded on an Oxford ISIS spectroscope attached to the microscope for composition analysis. X-Ray photoelectron spectroscopy (XPS) was taken on an ESCALab MKII X-ray photoelectron spectrometer, using Al K α X-ray as the excitation source. The binding energies obtained in the XPS analysis were calibrated against the C1s peak at 284.6 eV.

Results and discussion

In the developed Ullmann-reaction synthetic route, four typical III–V compounds can be obtained. For the synthesis of InP and InAs nanocrystals, the chemical reactions employed are as follows:

$$2In + 2PPh_3 \rightarrow 2InP + 3Ph-Ph$$
(2)

$$2In + 2AsPh_3 \rightarrow 2InAs + 3Ph-Ph \tag{3}$$

The two reactions are feasible thermodynamically. For $G^{\circ} =$ $H^{\circ} - T \cdot S^{\circ}$, in an isothermal process (T is constant), $\Delta_r G^{\circ} =$ $\Delta_r H^\circ - T \cdot \Delta_r S^\circ$, and $\Delta_r G^\circ$ is determined by $\Delta_r H^\circ$, $\Delta_r S^\circ$ and T. If the temperature (T) is low or not very high, the influence of $T \cdot \Delta_r S^\circ$ on the above equation is rather small, and the value of the first term on the right side of the equation dominates that of $\Delta_r G^{\circ}$. Therefore, the value of $\Delta_{\rm r} G^{\circ}$ approaches that of $\Delta r H^{\circ}$. Ignoring the influence of $T \cdot \Delta_r S^\circ$ on the reaction, we have calculated the Gibbs energy change $(\Delta_r G^\circ)$ in these reactions at 25 °C (and even up to 400 °C).⁴⁰ For the synthesis of InP, the Gibbs energy change of reaction 2 is calculated as follows: $\Delta_r G^\circ = \Delta_r H^\circ - T \cdot \Delta_r S^\circ \approx$ $\Delta_{\rm r} H^{\circ} = \sum \Delta_{\rm f} H^{\circ}_{\rm (products)} - \sum \Delta_{\rm f} H^{\circ}_{\rm (reactants)} = -343.6 \text{ kJ mol}^{-1}$, while the change in the Gibbs energy in reaction 3 for the synthesis of InAs is about -439.0 kJ mol⁻¹. The Gibbs energy changes in these synthetic reactions are rather negative, which implies a vigorous tendency for reactions (2) and (3) to progress towards the right side. Similarly, the Gibbs energy changes of the reactions to GaP and GaAs are also negative, and the corresponding reactions of (4) and (5) (as shown below)

$$2Ga + 2PPh_3 \rightarrow 2GaP + 3Ph - Ph \tag{4}$$

$$2Ga + 2AsPh_3 \rightarrow 2GaAs + 3Ph - Ph$$
⁽⁵⁾

can proceed toward the right side thermodynamically. It is concluded that a general approach could be proposed for the synthesis of group III–V semiconductor materials through such designed chemical reactions in sealed vacuum tubes under moderate conditions on the basis of the thermodynamic principle.

The XRD patterns of the as-synthesized products are shown in Fig. 1, which indicates that all the III–V products are of good

 Table 1
 Synthetic conditions of III–V nanocrystals with various morphologies and crystallographic phases^a

Precursor molar ratio of III to V	Conditions	Products	Morphologies of the products	Phases of the products
1 : 1.2 (In:P)	400 °C, 8 h	InP	NWs	ZB and W NWs
1:1(In:As)	370 °C, 24 h	InAs + As	NPs and NRs	ZB NPs and W segments
2:1 (In:As)	350 °C, 24 h	InAs	NPs and NRs	ZB NPs and W segments
1:1.2 (Ga:P)	380 °C, 12 h	GaP	NPs and NWs	ZB NPs and W NWs
1:1(Ga:As)	380 °C, 24 h	GaAs + As	NPs	ZB NPs
2:1 (Ga:As)	360 °C, 24 h	$GaAs + As_{trace}$	NPs	ZB NPs
3 : 1 (Ga:As)	360 °C, 24 h	GaAs	NPs	ZB NPs

" NWs, NPs and NRs denote nanowires, nanoparticles and nanorods, respectively.



Fig. 1 XRD patterns of (a) the InP sample synthesized at 400 $^{\circ}$ C for 8 h; (b) the InAs sample synthesized at 370 $^{\circ}$ C for 24 h; (c) the GaP sample synthesized at 380 $^{\circ}$ C for 12 h; and (d) the GaAs sample synthesized at 380 $^{\circ}$ C for 24 h. The diffraction peaks marked with asterisks are from the W structure.

crystallizability. Fig. 1a and b are the XRD patterns for the InP and InAs products synthesized at 400 °C for 8 h and at 370 °C for 24 h, respectively. It is interesting to note that there are weak W structured diffraction peaks besides the ones of the main ZB phase presented in the patterns, which indicates that metastable W InP and InAs were produced under current moderate conditions. However, there is not any W GaP (Fig. 1c) and GaAs (Fig. 1d) observed for the GaP and GaAs samples synthesized at 380 °C for 12 h and at 380 °C for 24 h, respectively, under the limit of detection of the diffractometer and there is only ZB GaP and GaAs detected (Fig. 1c and d). Meanwhile, there is some As impurity existing in the InAs and GaAs products because of the observation of extra diffraction peaks of As in the patterns (Fig. 1c and d). Elemental As impurity in the arsenides results from the pyrogenation of AsPh₃ at 350-400 °C. In the synthesis, increasing the molar ratios of III to V can eliminate As impurity in the products. As shown in Fig. 2, pure InAs and GaAs products were obtained by changing the molar ratios of reaction precursors with the excess IIIA metals, and detailed experimental conditions can be seen in Table 1. It is also noted that there is a broad hump for both GaP and GaAs samples near the $36^{\circ} 2\theta$ angle in their corresponding XRD patterns (Fig. 1c and 2b). The origin of this hump is probably due to the generation of oxides (formation of Ga₂O₃) and amorphous materials, and the similar phenomena were reported previously in ref. 21.

The III–V semiconductor nanocrystals synthesized *via* the present approach displayed a series of diverse morphologies (shown in Table 1) although we intended to obtain 1D nanostructures. The detailed investigations were demonstrated as follows. TEM images (Fig. 3a and b) showed that the InP products



Fig. 2 XRD patterns of (a) the pure InAs sample produced using In and AsPh₃ taken in a ratio of 2:1; and (b) the pure GaAs sample produced using Ga and AsPh₃ with a ratio of 3:1.

displayed a 1D wire-like morphology, and the studies of ED and HRTEM (Fig. 3c) established that the presence of W diffraction peaks in the XRD pattern (Fig. 1a) was due to the production of W InP nanowires, and that these W InP nanowires were of a single-crystal nature in the diameter range of 30–150 nm. It is well-known that InP is stable in ZB structure, especially in the bulk,⁴¹⁻⁴⁵ and the sequence of stabilization for ZB structured MP (M=Ga, Al, In) is on the order of GaP < AIP < InP.⁴⁴ The structural preference denotes the strong trend in the growth of InP with



Fig. 3 (a) TEM image of the InP nanowires synthesized at 400 $^{\circ}$ C for 8 h; (b) TEM images of typical single-crystal W InP nanowires with the various diameter of 31 nm, 80 nm and 110 nm, respectively; (c) HRTEM image and ED pattern (the inset) recorded on W InP nanowires; (d) HRTEM image and ED pattern (the inset) recorded on ZB InP nanowires.

ZB structure, and it is difficult to obtain W structured InP single crystals because of the high thermodynamic stability of ZB InP.41-45 In fact, many methods reported the production of InP nanowires with the ZB phase. Recently, it is noted that InP nanowires with W structure have been reported growing on InP(111)A substrates by a selective area metalorganic vapor phase epitaxy (MOVPE) process.⁴⁶ However, the W structure of InP should be further confirmed since the given ED pattern of the InP nanowires in ref. 46 is likely to be indexed as the diffraction spots of ZB structure along the [112] projection rather than the [010] projection of W structure. More recently, ultrafine InP nanowires fabricated by MOVPE^{47,48} take ZB structure with many rotational twin blocks consisting of W segments along the <111> growth directions. A recent theoretical calculation suggests that the stability trend of ZB and W structured nanowires depends on the diameter of nanowires, and W nanowires are stabilized in small diameter (<32 nm for InP).⁴⁵ It is very significant to obtain metastable W InP single-crystal nanowires with large diameter from the reaction of indium nanoparticles with PPh₃, which is clearly confirmed by XRD, ED and HRTEM in the present work. The synthesis of single-crystal W InP nanowires with large diameters up to 150 nm will promote the studies on the polytypism and the relative stability between ZB and W structures of InP crystals. The investigations of XRD and HRTEM also demonstrated that the ZB InP nanowires are of high crystallizability and single-crystal nature (Fig. 3d).

Fig. 4 demonstrates typical TEM images of the InAs products, showing that the products are in the shapes of both nanoparticles and nanorods. The analysis of ED and HRTEM indicated that InAs nanoparticles took the ZB phase, and that W structured segments, stacking faults and rotational twins were often present in the InAs nanorods along the growth direction, which resulted in the appearance of W diffraction peaks in the XRD pattern of the InAs sample. Fig. 4c-f shows ED patterns and HRTEM images taken from InAs nanorods. The ED pattern (Fig. 4c) clearly presents one set of basic diffraction spots and two sets of additional spots. The basic set is indexed as the ZB InAs diffraction pattern viewed along the [110] direction. One set of additional spots corresponds to the ZB InAs (111) twinning diffraction pattern viewed along the [110] direction, and the other set corresponds to the W InAs diffraction pattern viewed along the [2110] direction (Fig. 4c). The corresponding HRTEM image is shown in Fig. 4d. Fig. 4e is the TEM image and ED pattern of another InAs nanorod. The ED pattern can be well indexed as the ZB (111) twinning diffraction pattern projected along the [110] direction, which indicates that the InAs nanorod consists of many rotational twins. The corresponding HRTEM image is shown in Fig. 4f, and it clarifies that the InAs nanorods comprise many W structured segments, stacking faults and rotational twins along the growth direction (the [111] direction). The special microstructures in the InAs nanorods can be attributed to the small energy difference between the W and ZB structures (ΔE_{W-ZB}). According to the recent theoretical calculation,⁴⁵ the ΔE_{W-ZB} of InAs nanowires will become smaller than that of the bulk InAs, which might cause the W structure incorporating ZB structured nanowires. At the same time, the current synthetic conditions, for example, the low temperature of 320-380 °C and low pressure in sealed vacuum tubes, facilitate the growth of metastable W structured segments in the InAs nanorods. The observation of such microstructures in the present work is close to the literature reported previously,45,49



Fig. 4 (a) TEM image of the as-synthesized InAs nanoparticles; (b) TEM image of InAs nanorods; (c) ED pattern and (d) HRTEM image of a typical InAs nanorod; (e) TEM image and ED pattern (the inset) of another individual InAs nanorod; (f) HRTEM image recorded on the InAs rod shown in (e), from which we can see that rotational twins dominate in the InAs nanorod along the growth direction (the [111] direction).

The similarly-relevant reasons can also induce the growth of singlecrystal W InP nanowires in the synthesis of InP.

The purity and surface composition of the InP and InAs samples were analyzed with XPS. Fig. 5 shows the high-resolution XPS spectra of the P2p region from the InP products and the As 3d region from the InAs ones. In the P2p close-up spectrum, there are two obvious peaks. The one at 128.53 eV corresponds to P from InP, and the other one at 133.37 eV corresponds to P from oxidized P species. The P peak from InP is much stronger than that from oxidized species (Fig. 5a), demonstrating the high purity of the as-synthesized InP products. As shown in Fig. 5b, three kinds of As peaks appear in the As region of the InAs products. The peaks at 40.67 eV, 41.36 eV and 44.41 eV can well be indexed as the peaks of As from InAs,⁵⁰ elemental As and As₂O₃,⁵¹ respectively. The presence of As peaks from InAs and elemental As in the XPS spectrum agrees well with the XRD results (Fig. 1b).

TEM images of the as-synthesized GaP and GaAs nanocrystals with curved shapes, which are fused from nanoparticles, displayed in Fig. 6a and b. The composition of these nanocrystals was close to 1 : 1 by checking with EDX (see the ESI†). We note that there are a small amount of GaP nanowires in the GaP



Fig. 5 Higher resolution XPS spectra of (a) the P 2p region from the InP products; and (b) the As 3d region from the InAs products obtained using In : $AsPh_3 = 1 : 1$.



Fig. 6 TEM images of (a) the GaP sample, and (b) the GaAs sample; (c) TEM image of an individual W GaP nanowire; (d) HRTEM image and ED pattern (the inset) recorded on the GaP nanowire shown in (c).

products. The analysis of SAED patterns and HRTEM images shows that GaP nanowires take W structure and grow in the [0001] direction (shown in Fig. 6c and d), while the curved GaP nanocrystals take the ZB structure. Because of the low yield of W GaP nanowires there are no obvious diffraction peaks of W structure observed in the XRD pattern (Fig. 1c) for the as-synthesized GaP sample. Moreover, no typical GaAs nanowires or nanorods were detected by TEM investigations. The low yields of 1D GaP and GaAs nanostructures are probably relevant to the large size and the poorly catalytic activity of commercial metallic gallium, while nanoscale metallic indium as a catalyst performs better for the anisotropic growth of 1D InP crystallites^{28,29} and other nanostructures.³¹

In the synthetic procedures, new-prepared metallic indium nanoparticles were used to synthesize InP and InAs since the indium nanoparticles with high reactivity can induce the synthesis to proceed sufficiently. However, it is difficult to prepare metallic gallium within the nanometer scale except a recent vapor route³¹ because of the too low melting point of gallium. In the route, commercial gallium was used for the synthesis of GaP and GaAs, and excess gallium was employed for the synthesis of GaAs nanocrystals to make the reaction progress effectively (see Table 1). It is also found that longer reaction time was required for the synthesis of GaP and GaAs. The reaction temperature of 320-400 °C was chosen for the synthesis of III-V nanocrystals, and a high temperature above 420 °C will lead to lots of amorphous carbon in the products, while at the low temperature below 320 °C the synthetic reactions can not be performed sufficiently, and will lead to the formation of amorphous indium and gallium pnicogenides mixed with the final products.

The investigations also showed that the degree of the difficulty in the synthesis of III–V compounds *via* the present synthetic route is in the following order: InP > InAs and GaP > InP. This trend could be approved with some designed experiments, determined by XRD. Fig. 7a is the XRD pattern of the products synthesized from the new-prepared indium nanoparticles reacting with the mixture of PPh₃ and AsPh₃, where the molar ratio of PPh₃ to AsPh₃ is 4 : 1. The XRD pattern indicates that InAs dominates



Fig. 7 (a) XRD pattern of the products synthesized from the reaction of new-prepared indium nanoparticles with the mixture of PPh₃ and AsPh₃ with the molar ratio of 4 : 1. The inset is the enlarged part of the XRD pattern from 20° to 30° (2 θ), indicating that InAs dominates the products; (b) XRD pattern of the products obtained from the reaction of PPh₃ with the mixture of metallic In and Ga with the molar ratio of 1 : 1.

the products, which means that the synthesis of InAs is much easier than that of InP. Basis on the thermodynamic calculations, the trend in the Gibbs energy changes of the reactions for the synthesis of InP and InAs is $\Delta_r G^\circ$ (-439.0 kJ mol⁻¹ at 25 °C)_{InAs} < $\Delta_r G^\circ$ (-343.6 kJ mol⁻¹ at 25 °C)_{InP}. The experimental results well match with the thermodynamic calculations. We also find that it is more difficult to obtain GaP than InP, which can be confirmed by the XRD pattern of the products obtained from the reaction of PPh₃ with the mixture of metallic In and Ga with the equal molar ratio (shown in Fig. 7b). The degree of the difficulty in the synthesis of III–V compounds can be summarized as follows: GaV > InV and IIIP > IIIAs (III = Ga, In, and V = P, As). Interestingly, this order is also consistent with the trend in bond energies (E_b) of group III–V compounds:⁵² Ga–V > In–V and III–P > III–As (III = Ga, In, and V = P, As).

In the present process, the formation of 1D InP, InAs and GaP nanostructures is attributed to the solution-liquid-solid (SLS) growth mechanism^{6,26-29,35-38}, due to the metallic droplets of metals existing in the process, and the nanocrystals with W structure or segments are resulted from the kinetic growth under moderate conditions along with the use of PPh₃ and AsPh₃. At temperatures of 320-400 °C, metallic indium and gallium become melting droplets, and they act as not only reactants but catalysts in the growth of 1D nanostructures. As reactants, the metals serve as the precursors for the synthesis of III-V nanocrystals as reaction performed,²⁶⁻²⁹ and as catalysts, they confine the growth of InP, InAs or GaP nanocrystals elongated along a specific direction to form 1D nanostructures based on the SLS growth model.^{6,26–29,35–38} Meanwhile, PPh₃ and AsPh₃ with the high steric effects⁵³ can affect the shape and crystallographic phase of InP, InAs and GaP nanocrystals with favorable anisotropic shapes. Previously, trioctylphosphine (P(C8H17)3, TOP) and trioctylamine (N(C₈H₁₇)₃, TOA) were often employed as additives to direct the growth of semiconductor nanocrystals with controllable size, shape and phase in the synthesis,8-12,28,29,32,54 and group II-VI and III-V nanostructures could be well tuned through the use of trialkylphosphines based on the control of these additives with specific steric effects.^{6,8-12,27-29,54-57} For another example, GaP nanorods were synthesized with W structure along with nanospheres with ZB structure.⁵⁴ The phase transformation from the ZB GaP to the W structure was kinetically affected by using different stabilizers such as TOA and hexadecylamine (HDA) with diverse steric effects.⁵⁴ Furthermore, trialkylphosphines and their similarities prove to be useful pnicogen sources for the synthesis of group III-V nanocrystals.^{6,8-12,27-29,32-34,58} The configurations of PPh₃ and AsPh₃ used in the present route are close to their similarities such as TOP, TOA, and etc., and they will further confine the growth of 1D nanostructures by suppressing atomic processes to metastable structure due to their highly steric effects besides the directing effects of the catalyst of metallic droplets in the SLS growth regime. It is concluded that the steric effects of the VA precursors (PPh₃ and AsPh₃) along with the low synthesis temperatures and pressures in sealed vacuum tubes cooperatively arouse nanocrystals growing in the metastable W phase from the aspect of kinetics. In addition, the viscous liquid consisting of unreacted PPh₃ or AsPh₃ and byproducts including biphenyl, terphenyl, and so on³³ also played important roles in the growth of 1D nanostructures with metastable W structures, rotational twins and stacking faults, since mass transfer in crystal growth is quietly limited in a high viscous system.⁵⁹⁻⁶¹ The as-synthesized III–V nanocrystals have broad size distributions, which can be ascribed to heterogeneous nucleation and catalysts of metal droplets with a diverse size. It is no doubt that the current work provide an alternatively creative route to group III–V semiconductors and relevant compounds although the improvements on the controllable synthesis along with their properties are needed in the coming investigations.

Conclusions

In summary, a new general strategy was put forward for the synthesis of III-V semiconductor nanocrystals through a developed Ullmann reaction from metallic indium or gallium with PPh₃ or AsPh₃ in evacuated sealed quartz tubes at 320-400 °C for 8-24 h. These synthesis reactions are thermodynamically feasible and easy to be realized kinetically, by which InP, InAs, GaP and GaAs nanocrystals have successfully been synthesized. The investigations of XRD, ED and HRTEM established the presence of metastable structures of W InP, InAs and GaP, which was induced by the high steric effects of PPh₃ and AsPh₃ as well as the low temperatures and pressure employed. It was found that the tendency in difficulty for the synthesis III-V semiconductor nanocrystals was as follows: IIIP > IIIAs (III = In, Ga) and GaV > InV(V = P, As). This work offered a good candidate for the studies on the polytypism and the relative stability between ZB and W phases of III-V semiconductors, and the employment of low temperature, sealed vacuum tubes and stable pnicogen precursors (PPh₃ and AsPh₃) with high safety largely simplified the synthetic procedures. The present synthetic strategy can be easily extended to synthesize other phosphides and arsenides, and other III-V semiconductors such as GaN, InN and InSb from precursors of NPh₃, SbPh₃, or even other triarylpnictines, and it would promote the development of methodologies for the synthesis of compound semiconducting nanomaterials.

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