Benzene-thermal Route to InP and InAs Nanocrystals Using Triphenylphosphine and Triphenylarsine as Pnicogen Sources

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Nanocrystalline InP and InAs were solvothermally synthesized by the reaction of newly reduced indium with triphenylphosphine (PPh_3) and triphenylarsine ($AsPh_3$) in benzene. The products were characterized by XRD, TEM, and EDX. PPh_3 and $AsPh_3$ with high safety as excellent P and As sources will provide a novelly alternative synthetic route to III–V semiconductor compouds.

Recently, group III–V semiconductor nanocrystals have gained considerable attention because of their properties superior to those of Si and group II–VI compounds in many ways as well as their potential applications in electronics, optoelectronics, nanodevices, and sensors.[1–4] However, the preparation of group III–V nanocrystals is largely restricted owing to numerous difficulties mainly relavant to their greater degree of covalent bonding and less-available precursors of pnicogens in comparison to those of II–VI materials. Up to now, many efforts have been paid for the fabrication of III–V nanostructures and some strategies have been developed, for instance, metal–organic chemical vapor deposition (MOCVD),[5] metal–organic vapor-phase epitaxy (MOVPE),[6,7] laser-assisted catalytic growth (LCG),[8] and nanocrystal-seeded growth,[9,10] along with solution-based methods.[11–14]

It is noticeable that a key focus of most of the above studies is how to gain group V elements (N, P, As, and Sb) properly from the reaction precursors, such as NH_3, EH_3, $(Na/K)_3E$, ECl_3 ($E = P$ and As), Li_3N, As_2O_3, P_4 (yellow), As powder, and organic compounds with elemental pnicogens. It is a smart pathway to gain V elements from organic compounds to prepare III–V semiconductor nanocrystals.[5,6,10–12] Metal–organic compounds, however, are usually of high toxicity and unstable in air, which arouses many difficulties in the synthesis, for example, the absolutely nonaqueous and nonoxygen system. Triphenylphosphine (PPh_3) with little toxicity and high safety is one of widely used compounds in chemistry, and it can be used as an available precursor of the novel P source for the preparation of III–P semiconductor nanocrystals. On the basis of the idea, recently, we have successfully prepared InP and GaP nanocrystals by commercial metal In and Ga reacting directly with PPh_3.[15]

Here, we developed the above idea, and prepared InP nanocrystals by the reduction of $InCl_3{\cdot}4H_2O$ with PPh_3 in the presence of KBH_4 in benzene solution at 350–380 °C. The developed method involved newborn metallic indium acting actively with PPh_3 to form nanocrystalline InP, and the whole reaction can be expressed as follows:

$$\begin{aligned}&2InCl_3{\cdot}4H_2O + 6KBH_4 + 2PPh_3\\&\rightarrow 2InP + 6KCl + 6BH_3 + 3H_2 + 8H_2O + 3Ph\text{–}Ph.\end{aligned} \qquad (1)$$

Meanwhile, InAs nanocrystals are also obtained via the benzene-thermal route by replacing PPh_3 with $AsPh_3$. We believe that it will be a novel and wide way to prepare III–V semiconductor materials in nanoscale by gaining V elements from novel organic compounds such as PPh_3 and $AsPh_3$.

Typically, 0.150 g (0.5 mmol) of analytically pure $InCl_3{\cdot}4H_2O$, 0.086 g (1.5 mmol) of KBH_4, and 1.000 g (4 mmol) of PPh_3 were added into 2–5 mL of benzene in a quartz container with a 20-mL volume, and the container was sealed in a autoclave, kept at 350–380 °C for 8–12 h, finally cooled to the room temperature on standing. The products obtained were washed with benzene, absolute alcohol, and distilled water, respectively. For detailed investigations, the products were divided into two parts: one part was washed with 1 M HCl and the other not, and then dried in vacuum at 60 °C for 4 h.

The XRD pattern reveals the production of InP from PPh_3. As shown in Figure 1a for the sample obtained after 1 M HCl treatment, the pattern can be well indexed to zinc-blend (ZB) phase InP with a lattice parameter $a = 5.861$ Å (JCPDS File No. 73-1983), which suggests that pure InP can be obtained in the present route. There are not any other impurities detected in the product. It is noted that metallic indium is mixed with the InP product before the sample was treated with 1 M HCl solution, which is confirmed by the XRD pattern shown in Figure 1b. The result indicates the presence of newly reduced indium in the synthesis. The synthetic route of InP is successfully employed to synthesize zinc-blend InAs nanocrystals by substituting $AsPh_3$ for PPh_3, though the product contains small amount of elemental As (Figure 1c). Elemental As may be produced by pyrogenesis from $AsPh_3$. According to the conversion of indium, the yield of InP is about 70%, and that of InAs is 85%.

TEM image of the InP sample is shown in Figure 2a, and the sample appears in irregular particles. Figure 2b demonstrates a magnified TEM image for an individual InP nanocrystal, and the corresponding ED pattern (inset of Figure 2b) confirms that

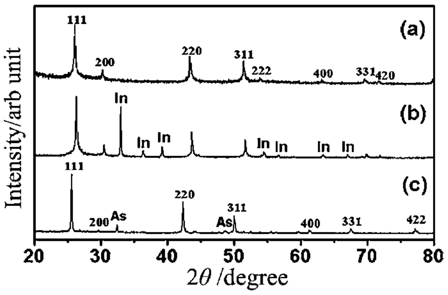

Figure 1. XRD patterns of the products: a) pure InP, after 1 M HCl treatment; b) InP with In before washing with 1 M HCl; c) Crystalline InAs with elemental As after washing with 1 M HCl.

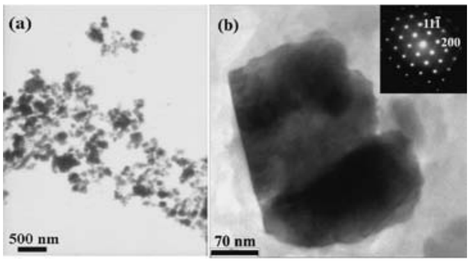

Figure 2. a) TEM image of the InP products; b) High-magnified TEM image of an individual InP nanocrystal, and the ED pattern (the inset) viewed along the [011] orientation.

the InP nanocrystal is in zinc blende form with single-crystal nature. Meanwhile, the ED pattern also reveals that the lattice spacing of 3.38 Å well agrees with the interplanar distance of {111} planes of zinc blende InP. The composition of the InP nanocrystals was checked by energy-dispersive X-ray spectroscopy (EDXS), which shows the presence of In and P with a ratio of 1.08:1.00 for the InP product. The composition of the InP nanocrystals is close to stoichiometric InP except for a slight excess of indium, which verifies the formation of InP in the benzene-thermal route. The obtained InAs nanocrystals also show irregular shape in TEM image (Figure S1, see Supporting Information).[16] In addition, the optical properties of both InP and InAs nanocrystals are investigated (Figure S2).

Analysis of the XRD patterns (Figures 1a and 1b) shows two basic steps involved in the present synthetic route. The first step is to reduce $InCl_3$ into active elemental metal indium in situ according to eq 2 or 3, and secondly, newborn indium can actively react with PPh_3 or $AsPh_3$ to form InP or InAs nanocrystals in benzene by the benzene-thermal reaction in eq 4.

$$2InCl_3 + 6KBH_4 \rightarrow 2In + 6KCl + 6BH_3 + 3H_2, \quad (2)$$

$$2InCl_3 + 3Zn \rightarrow 2In + 3ZnCl_2, \quad (3)$$

$$2In + 2PPh_3/2AsPh_3 \rightarrow 2InP/2InAs + 3Ph\text{–}Ph. \quad (4)$$

The merit of the presently developed method is that the newborn metal indium with a higher activity than bulk indium enhances the formation of crystalline InP and InAs. When bulk metal indium was directly used in the benzene-thermal route at 380 °C, it is difficult to obtain nanocrystalline InP and InAs. As we known, III–V materials are highly covalent nonmolecular solid-state compounds with weaker polarity compared with II–VI compounds, so the selection of nonpolar benzene solvent could provide a favorable reaction medium for the preparation of InP and InAs nanocrystals as well as benzene is a good solvent for PPh_3 and $AsPh_3$. In addition, the high pressure self-generated in the sealed benzene-thermal synthetic system can also promote the crystallization of InP and InAs at the relative low temperature of 350–380 °C. In the process, no extreme conditions such as an absolutely nonaqueous and nonoxygen environment are required because of the use of reductants. The reducing environment caused by KBH_4 (or Zn powder) keeps the products away from being oxidized. Besides, the use of PPh_3 can effectively avoid the presence of PH_3, $(Na/K)_3P$, PCl_3, or yellow phosphorus with poor stability and high toxicity. As the novel P and As sources, both PPh_3 and $AsPh_3$ are stable in air, which can largely simplify the synthetic procedures and promote the advance in the preparation of phosphides and arsenides.

In conclusion, nanocrystalline InP and InAs have been successfully synthesized via the reduction of $InCl_3 \cdot 4H_2O$ with PPh_3 and $AsPh_3$ in the presence of KBH_4 and Zn powder in benzene solvothermally. The use of PPh_3 and $AsPh_3$ provides excellent P and As sources for the preparation of group III–V phosphides and arsenides. The current route has been applied for the other III–V semiconductors such as InN, InSb, GaP, and GaAs, and the studies are in progress. The synthesis offers us a pathway to synthesize solid-state semiconductor materials by obtaining the required elements from novel organic compounds. It is confidently believed that the adoption of this pathway will further bring new opportunities to the preparation of III–V group semiconductor heterostructures and alloys, even some II–VI or IV–IV compounds.

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16 Supporting Information is available electronically on the CSJ Journal Web site. http://www.csj.jp/journals/chem-lett/.