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A low-temperature route to InP nanocrystals

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Nanocrystalline InP was prepared at temperatures of 80–160 °C through a novel route:

$$4InCl_3 + 12KBH_4 + P_4 \xrightarrow{en} 4InP.$$

Mean crystallite dimensions of 11.3–20 nm were determined from X-ray powder diffraction. Transmission electron microscopy images showed that the products were 15–20 nm spherical grains when prepared at 120 °C and 150 × 1500 nm rod-like grains at 160 °C. The reaction proceeds through a metallic indium intermediate and a solution–liquid–solid mechanism is proposed for the one-dimensional growth. The products were also investigated by UV/vis absorption, photoluminescence, Fourier-transform IR, and X-ray photoelectron spectroscopy.

Introduction

The discovery of markedly different properties from the bulk materials and the promise of exploiting these properties for making devices have led to widespread research activity in the field of nanocrystalline materials both on scientific and technological grounds.[1] While the II–VI materials such as CdSe and CdS have been extensively studied,[2,3] synthetic limitations have precluded similar treatment of other materials. However, synthesis and characterization of III–V semiconductor nanocrystals such as GaAs[4,5] and InP[6–12] have received renewed interest due to their technological importance. Nanocrystalline InP can be made by dehalosilylation of $InCl_3$ and $(Me_3Si)_3P$ with subsequent thermolysis at 650[6] or 200–400 °C.[7] Recently better quality materials have been prepared by thermolysis reactions in TOPO (tri-*n*-octylphosphine oxide) by Micic *et al.*,[8] which was further exploited by Alivisatos and coworkers[9] to synthesize monodisperse and soluble InP nanocrystals. Solution Phase Metathesis (SPM) of $InCl_3$ and $(Na/K)_3P$ can also be used to prepare InP nanocrystals, but annealing at higher temperature is required.[10] Very recently, Green and O'Brien[11] reported a direct and rapid synthesis of monodispersed InP quantum dots, but the crystallinity was not mentioned. A low temperature route to well crystallized InP nanoparticles was recently reported by Buhro and coworkers,[12] who obtained crystalline InP fibers at 111–203 °C, but extremely toxic PH_3 was used in the process. It is of interest to create synthetic routes for III–V semiconductor nanocrystals, using inexpensive chemicals and with a simple set-up. In this paper we describe a novel route to InP nanocrystals at temperatures as low as 80 °C, which is the lowest temperature reported for preparing crystalline InP up to now.[12]

KBH_4 and its derivatives have been used to prepare finely divided powders of metals and alloys by reducing metal salts in organic solvents such as THF and hydrocarbons:[13]

$$uMX_v + vM'(BR_3H)_u \xrightarrow{THF} uM + vM'X_u + uvBR_3 + \frac{uv}{2} H_2\uparrow$$

In this paper, we extend this method to prepare compounds, rather than elements or alloys, in ethylenediamine by modifying the pathway as follows:

$$4InCl_3 + 12KBH_4 + P_4 \xrightarrow{en} 4InP + 12KCl + 12BH_3 + 6H_2$$

Experimental

All reagents were of analytical grade or better and used without further purification. Reactions were carried out in a Teflon-lined autoclave. 40 ml ethylenediamine, 1.24 g (10 mmol) of yellow phosphorus, 1.11 g (5 mmol) of $InCl_3$ and 1.6 g KBH_4 (30 mmol) were placed in a 50 ml Teflon-lined autoclave kept at 80, 120, 150 or 160 °C for 16 h, and then cooled to room temperature naturally. The mixture turned black due to the formation of InP precipitates. The products were filtered out, washed with absolute alcohol and water, and then dried in vacuum at room temperature for 30 min.

XRD patterns were obtained on a Japan Rigaku D/Max γA rotating anode X-ray diffractometer with Ni-filtered Cu-Kα radiation ($\lambda = 1.54178$ Å). TEM measurements were made on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV.

X-Ray photoelectron spectra (XPS) were recorded on an ESCALab MKII instrument with Mg-Kα radiation as the exciting source. The binding energies obtained in the XPS analysis were corrected by referencing the C 1s peak to 284.60 eV.

The infrared (IR) spectra were recorded in the wavenumber range of 4000–500 cm^{-1} with a Nicolet Model 759 Fourier transform infrared (FTIR) spectrometer, using a KBr wafer.

Room temperature UV/vis absorption spectrum of the InP particles dispersed in water were recorded using a Shimadzu UV-240 UV/vis spectrophotometer. Room temperature photoluminescence (PL) spectra of the InP particles were recorded using a Hitachi 850 fluorescence spectrophotometer in reflection geometry.

Results and discussion

Reaction of $InCl_3$, yellow phosphorus and potassium tetrahydroborate at 80–160 °C in ethylenediamine resulted in black-brown precipitates. X-Ray powder diffraction (XRD) patterns (Fig. 1) of the samples agree well with the bulk InP reflections indicating the same cubic zinc blende lattice structure.[14] Average crystallite sizes estimated by the Scherrer equation based on the half-widths of XRD peaks increase with reaction temperature, *i.e.* 11.3 nm for 80 °C, 15 nm for 120 °C, 17.5 nm for 150 °C and 20 nm for 160 °C. Transmission electron microscopy (TEM) images for the samples prepared at 120 °C revealed discrete 15–20 nm sphere-like particles (Fig. 2A), which is a little larger than that from XRD. TEM for the sample prepared at 150 °C

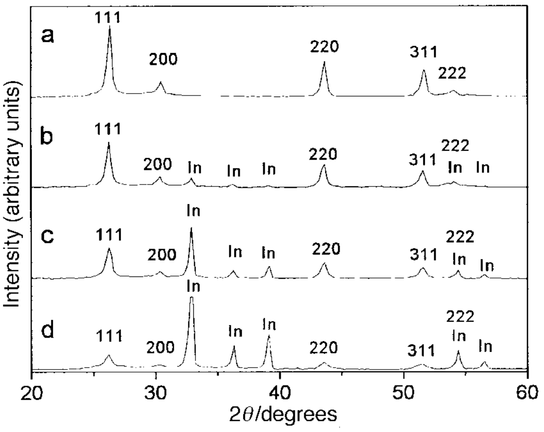

Fig. 1 XRD patterns of the product prepared at: (a) 160; (b) 150; (c) 120; (d) 80 °C.

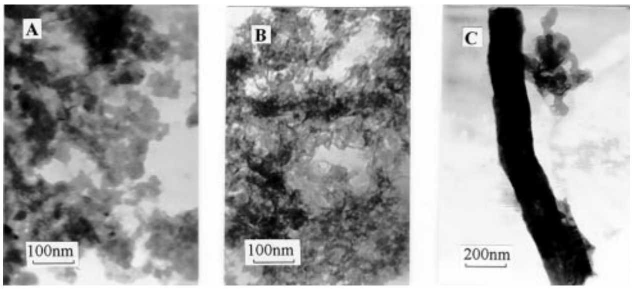

Fig. 2 TEM images for InP nanocrystals: (A) 120; (B) 150; (C) 160 °C.

showed aggregation of particles with irregular morphologies (Fig. 2B). A nanorod with a diameter of 150 nm and a length of more than 1500 nm was clearly seen for the sample prepared at 160 °C (Fig. 2C). More careful observation showed that the nanorod itself was composed of smaller particles.

The reaction temperature is a critical factor in this process. At room temperature the reaction did not initiate at all; at 80 °C there was much metallic indium and pure InP could not be obtained even when 2 M HCl was used to remove indium; at temperatures of 120–150 °C, pure InP could be obtained with HCl treatment; at 160 °C pure InP was obtained without HCl treatment. The relative intensity of the peaks in the XRD patterns showed that the indium content decreased with reaction temperature (Fig. 1). These facts led us to a possible mechanism as follows:

$$2\mathrm{InCl_3} + 6\mathrm{KBH_4} \xrightarrow{\mathrm{en}} 2\mathrm{In} + 6\mathrm{KCl} + 6\mathrm{BH_3} + 3\mathrm{H_2} \qquad (1)$$

$$4\mathrm{In} + \mathrm{P_4} \xrightarrow{\mathrm{en}} 4\mathrm{InP} \qquad (2)$$

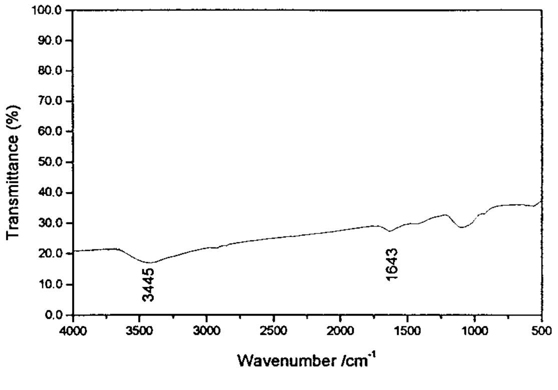

Fig. 3 IR spectrum of InP nanocrystals.

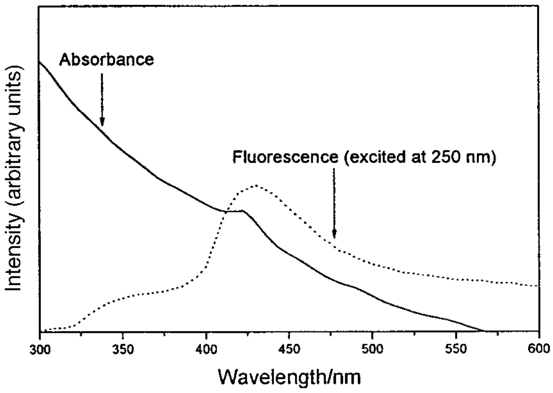

Fig. 4 Absorbance and photoluminescence (PL) spectra of InP nanocrystals prepared at 150 °C. The PL spectrum was taken in reflection geometry. The excitation wavelength for the emission spectrum was 250 nm.

Now all the above facts can be rationalized: at room temperature, even the first step can not take place; when the temperature is as low as 80 °C, the freshly formed indium agglomerated into indium drops and the phosphorus reacted on the surface to form InP ($T_{\mathrm{mp}} > 1000$ °C), which inhibited further reaction, so indium can not be completely removed by 2 M HCl. The newly formed indium is much more active and can be converted into InP completely at temperatures higher than 120 °C although bulk metal indium and P_4 were reported not to react at temperatures below the melting point of indium (156.4 °C).[12]

Among the three well known whisker-growth mechanisms, *i.e.* vapor–liquid–solid (VLS), vapor–solid (VS) and solution–liquid–solid (SLS), the SLS mechanism, which has been previously reported by Buhro and co-workers[12] in the preparation of InP fibers at temperatures of 111–203 °C, is most likely under the present conditions. The two cases both involved reactions in organic solvent, and trace indium existed in the products. Since the SLS mechanism can not function without liquid indium, reaction at temperatures below the melting point of indium (156.4 °C) should not give rod-like products. The failure to obtain any rod-like particles at 120 and 150 °C further confirmed the proposed mechanism (Fig. 2).

Ethylenediamine also played an important role in the formation of InP nanocrystals. Experiments showed that it could disperse yellow phosphorus to form a brown dispersion and readily dissolve KBH_4, so it could increase the surface area of reactants and promote the reaction at relatively low temperatures. When benzene was used as the solvent the reaction did not take place due to the poor solubility of KBH_4 in benzene; when pyridine was selected, some reactions took place, but the products have not been identified.

The IR spectrum (Fig. 3) of the products did not show any characteristic peaks of ethylenediamine, indicating that the ethylenediamine was at most weakly bonded to the surface and can readily be removed by washing with water. The broad absorption bands at 3445 and 1643 cm^{-1} in Fig. 3 were due to the absorbed water.

Fig. 4 shows the UV/vis absorption and photoluminescence (PL) spectra at room temperature of InP nanocrystals (diameter = 17.5 nm, prepared at 150 °C). The absorption spectrum was taken of an InP dispersion in water and showed an excitonic peak at about 420 nm, a significant blue shift from the bulk band gap of 1.35 eV (919 nm). The PL (excitation at 250 nm) was taken in reflection geometry and showed an emission band at 430 nm with a shoulder at 350 nm.

X-Ray photoelectron spectroscopy (XPS) was used to measure the elemental composition of the nanocrystals. A typical survey spectrum is shown in Fig. 5. The survey indicates the

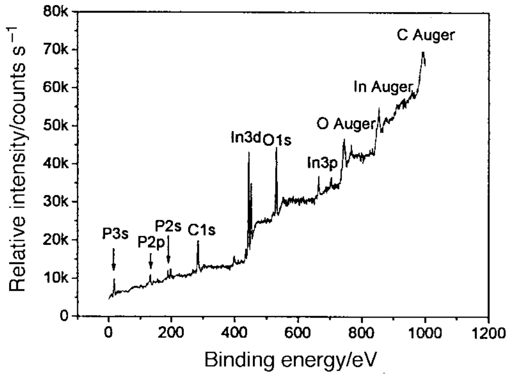

Fig. 5 XPS survey spectrum for InP nanocrystals prepared at 150 °C.

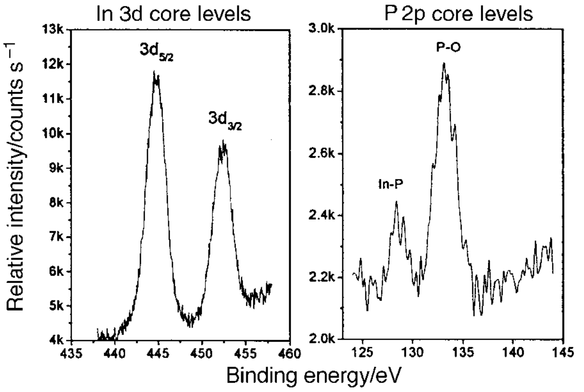

Fig. 6 High-resolution XPS scans of the In 3d and P 2p cores.

presence of In and P, as well as C from the reference and O from absorbed water. Higher resolution spectra were also taken of the In 3d region and P 2p region (Fig. 6). The indium core is spin–orbit split to 3d$_{5/2}$ and 3d$_{3/2}$ with the 3d$_{5/2}$ peak at 444.3 eV. The P 2p core shows two peaks, one at 128.0 eV corresponding to P from InP and the other at 132.8 eV corresponding to oxidized P species. Peak areas of these high-resolution scans were measured and gave an In : P ratio of 48 : 52 after correction for the relative cross-sections of In and P, thus we conclude that the nanocrystals are close to stoichiometric InP.

Conclusion

11.3–20 nm InP nanocrystals and 150 × 1500 nm nanorods were successfully synthesized *via* a novel reaction of $InCl_3$, P_4 and KBH_4 in ethylenediamine at temperatures of 80–160 °C. The reaction proceeds through a metallic indium intermediate and a solution–liquid–solid (SLS) mechanism is proposed for the one-dimensional growth.

Acknowledgements

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