

Hydrothermal Synthesis of InP Semiconductor Nanocrystals

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Pure InP nanocrystals were synthesized in aqueous ammonia (potassium stearate, $0.01 \text{ mol}\cdot\text{L}^{-1}$) at 170°C for 12 h. The X-ray diffraction pattern was of the cubic phase with lattice constant $a = 5.8523 \pm 5 \times 10^{-4} \text{ \AA}$. The secondary particles with 180 nm consisting of fine InP NCs with 15 nm in size were found from the transmission electron microscope images. The optimal reaction conditions were searched, and a possible reaction mechanism was discussed.

InP is an important direct-band-gap III-V group semiconductor because of its electronic properties and excellent lattice match with low-band gap alloys, which makes it attractive for applications in a wide range of electronic and opto-electronic devices.¹

InP quantum dots (QDs) exhibited unique optical and electronic properties due to quantum confined effects. In the past decade, many studies on the preparation of InP QDs have been reported, including colloid chemistry, molecular beam epitaxy (MBE), organometallic chemical vapor deposition (MOCVD), and physical vapor deposition. For avoiding complex reactions, toxic precursors and searching for milder preparation conditions, there have been considerable efforts to explore synthetic routes for InP nanocrystals (NCs) and QDs. They could be prepared by dehalosilylation of InCl_3 and $[(\text{CH}_3)_3\text{Si}]_3\text{P}$ in triethylphosphine oxide (TOPO) and subsequent thermolysis at 650°C ² or $200\text{--}400^\circ\text{C}$.³⁻⁵ Green and O'Brien reported a direct and rapid synthesis of monodispersed InP QDs by decomposing the complex $\text{In}[\text{P}(t\text{-Bu})_2]_3$ in 4-ethylpyridine at 167°C .⁶ Solution phase metathesis of InCl_3 and $(\text{Na/K})_3\text{P}$ could be used to prepare InP NCs, by annealing at higher temperature,⁷ similar reaction could be completed in solvothermal system at 180°C .⁸ Recently, a KBH_4 -reduction reaction was applied to the synthesis of InP NCs in solvothermal system at $80\text{--}160^\circ\text{C}$ ⁹ or by sonochemical process in benzene/ethanol mixed solvent at room temperature.¹⁰ All of the above methods were carried out in organic solvents.

In this letter, pure InP NCs of 15 nm were synthesized in aqueous ammonia (potassium stearate, $0.01 \text{ mol}\cdot\text{L}^{-1}$) at 170°C for 12 h. The InP NCs were characterized by XRD, XPS and TEM. The optimal reaction conditions (temperature, reaction time, the pH values, and surfactants) were searched, and a possible reaction mechanism was proposed.

In a typical procedure, $\text{InCl}_3\cdot 4\text{H}_2\text{O}$ (99.99%, 0.506 g, 1.726 mmol), excessive yellow phosphorous (99%, 1.24 g, 40 mmol), and potassium stearate ($\text{C}_{17}\text{H}_{35}\text{CO}_2\text{K}$, 98.0%, 0.161 g, 0.5 mmol) were added into 50 ml aqueous ammonia (25–28%, pH = 13.62), after stirred magnetically for 30 min, the reactant solution was transferred into a stainless Teflon-lined autoclave of 60 ml which was sealed and maintained at 170°C for 12 h, then the autoclave was cooled to room temperature on standing. The black precipitate was filtered and washed with

distilled water, diluted acetic acid, and then absolute alcohol, and dried in vacuum at 70°C for 2 h. The yield based on $\text{InCl}_3\cdot 4\text{H}_2\text{O}$ was about 80%.

The XRD¹¹ pattern of the as-prepared InP NCs was shown in Figure 1. All the peaks could be indexed as the cubic InP phase with lattice parameter $a = 5.8523 \pm 5 \times 10^{-4} \text{ \AA}$, which was close to the standard data (JCPDS PDF, No. 32-452, $a = 5.869 \text{ \AA}$). Employing the Debye-Scherrer formula,¹² the mean size of the InP NCs was estimated to be 15 nm from the half widths of the major diffraction peaks.

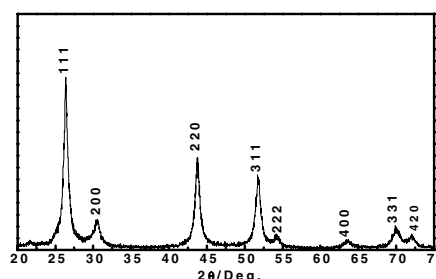


Figure 1. The X-ray diffraction (XRD) pattern of InP nanocrystals (170°C , 12 h, $\text{C}_{17}\text{H}_{33}\text{CO}_2\text{K}$, $0.01 \text{ mol}\cdot\text{L}^{-1}$).

The XPS¹³ of the as-prepared InP NCs were shown in Figure 2. The In core (Figure 2a) gave $3d_{5/2}$ (444.0 eV) and $3d_{3/2}$ (451.55 eV) peaks due to spin-orbit split. The P 2p core (Figure 2b) showed a peak at 128.8 eV and a shoulder at 129.3 eV, which were the characteristic of InP.^{5,14} The weak peak at 133 eV was assigned to oxidized P species, in this case PO_4^{3-} . The In : P ratio of 1.237 : 1 was calculated from the peak areas of In $3d_{5/2}$ at 444.0 eV and P 2p at 128.8 eV. This ratio indicated the formation of phosphates and/or oxides at the surface of InP NCs. In the C 1s region (not shown), the intensity of C 1s peak at 284.6 eV was on the contamination level, and a weak peak at 288.3 eV was observed, which was resulted from the carbon atom of carboxyl in $\text{C}_{17}\text{H}_{33}\text{CO}_2^-$. This implied that the surface of InP NCs was

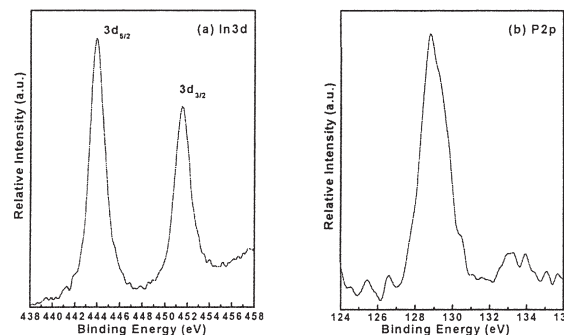


Figure 2. The X-ray photoelectron spectra (XPS) of InP nanocrystals (170°C , 12 h, $\text{C}_{17}\text{H}_{33}\text{CO}_2\text{K}$, $0.01 \text{ mol}\cdot\text{L}^{-1}$), (a) In 3d region, and (b) P 2p region.

capped with $C_{17}H_{33}CO_2^-$ ion. Other impurities such as chloride ion, potassium ion, elemental phosphorus, and nitrogen were not detected by the XPS.

Figure 3a shows the TEM¹⁵ image of the as-prepared InP NCs. Spherical secondary particles with 180 nm were found, which consisted of fine NCs with 15 nm in size. In the SAED pattern (Figure 3b), the concentric diffraction rings could be indexed outwards as 111, 220, and 311 diffractions, which indicated the nanocrystalline nature of the product.

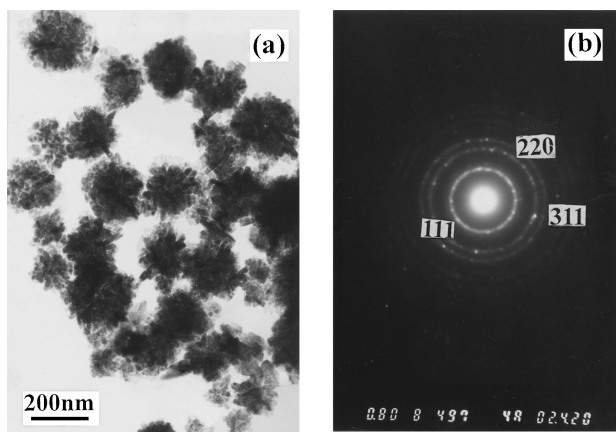
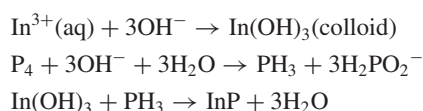


Figure 3. The transmission electron microscope (TEM) image (a), and selected area electron diffraction (SAED) (b) of InP nanocrystals (170 °C, 12 h, $C_{17}H_{33}CO_2K$, 0.01 mol·L⁻¹).

According to our 12 h-reaction results, the reaction temperature of 170 °C was approximately the lowest one to synthesize InP NCs. At lower temperature, 160 °C for example, cubic In(OH)₃ (JCPDS PDF No. 16–161) was found to be the exclusive phase by the XRD pattern of products. On the other hand, at 190 °C, spare In(OH)₃ coexisted with main product InP (about 30 nm), which indicated that the higher temperature would speed the growth of InP NCs and its hydrolysis as well.

Without potassium stearate, the InP NCs (about 20 nm) evolved after heating for 3 h at 170 °C, and from 3 to 12 h, no obvious nanocrystal growth was detected from the breadth of the XRD peaks of the products. When extending the reaction time to 24 h, well-crystalline InP NCs with about 30 nm in size and a trace of In(OH)₃ were obtained. Therefore, the reaction period of 3–12 h at 170 °C not only ensured the completeness of preparation reaction but also suppressed the hydrolysis of products.

The pH value of the aqueous ammonia system was another key factor for synthesizing InP NCs. In our experimental system (170 °C, 12 h), the end pH value decreased to 11.20 from the initial 12.18 owing to the disproportionation of P₄ molecules.^{16–18} Within this pH range, insoluble In(OH)₃ ($K_{sp} = 1.3 \times 10^{-37}$) absorbed OH⁻ to form colloidal solution which was an ideal indium source for InP NCs.¹⁹ Therefore, a possible mechanism was proposed as follows,



When the initial pH was less than 11.2, yellow phosphorous remained in the final products and the absence of InP indicated that the disproportionation of P₄ molecules did not occur.

Increasing pH to 13.85 by adding aqueous NaOH solution, however, resulted in InP NCs with larger size (about 50 nm).

In the existence of the surfactant potassium stearate (0.01 mol·L⁻¹), the InP NCs of 15 nm were obtained at 170 °C for 12 h. With other surfactants, however, such as sodium dodecylbenzene sulfonate ($C_{12}H_{25}C_6H_4SO_3Na$), and cetyl trimethyl ammonium bromide ($C_{16}H_{33}N(CH_3)_3Br$), no obvious confined effect on the size of InP NCs was observed. According to the XPS result of C1s region and the TEM image, the function of potassium stearate could be considered as to passivate the surface of InP NCs to confine nanoparticle growth (from 20 nm to 15 nm). Further researches on effective surface passivation of InP NCs in hydrothermal conditions were underway.

In summary, pure InP NCs of 15 nm were prepared in aqueous ammonia (potassium stearate, 0.01 mol·L⁻¹) at 170 °C for 12 h. Searches on reaction conditions revealed that, at 170 °C, for 3–12 h, and in aqueous ammonia of pH > 11.2, InP NCs of 20 nm could be synthesized and stably exist.

Since most of previous preparation methods for InP NCs and QDs were carried out in organic solvents systems, our results of hydrothermal synthesis of InP NCs supplied possibility for synthesizing non-oxides nanocrystals in hydrothermal systems.

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