

Low Temperature Synthesis of InP Nanocrystals

Thesis submitted to Sikkim University

for the award of the degree of

MASTER OF PHILOSOPHY



SIKKIM UNIVERSITY

[A Central University Established By an Act of Parliament, 2007]

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DECLARATION

I declare that the thesis entitled "Low temperature synthesis of InP nanocrystals" submitted by me for the award of **Master of Philosophy (M.Phil.)** degree of Sikkim University is my own work. The content of this thesis is based on experiments performed by myself under the supervision of Dr. Sudarsan Tamang. No part of the thesis has been submitted for any other degree, diploma, associate-ship, fellowship.

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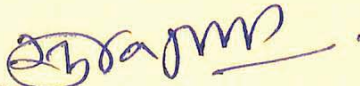
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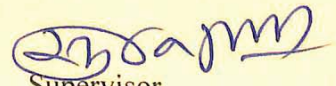
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Certificate

This is to certify that the thesis entitled "Low temperature synthesis of InP nanocrystals" submitted to the **SIKKIM UNIVERSITY** in partial fulfillment of the requirements for the degree of **Master of Philosophy in Chemistry** is a result of *bona fide* research work carried out by **Mr. Pulakesh Das** under my supervision. No part of the thesis has been submitted for any other degree, diploma, associate-ship, fellowship.

All the assistance and help received during the course of the investigation have been duly acknowledged by him.

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*I dedicate this thesis to my Parents,
Brother and Sister.*

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Table of Contents

Abbreviations	i
Symbols	ii
I. Introduction	1
1.1 Introduction	2
1.2 Quantum Dots	2
1.2.1 Definition	2
1.2.2 Properties of quantum dots	3
1.2.2.1 Quantum confinement effect	3
1.2.2.2 Optical properties of semiconductor nanoparticles	4
1.2.2.2.1 Absorption	4
1.2.2.2.2 Photoluminescence	4
1.2.2.3 Crystal structure	5
1.3 Synthesis of indium phosphide (InP) NCs	6
1.3.1 High temperature synthesis route	7
1.3.2 Low temperature synthesis route	8
1.4 References	11
II. Materials and methodology	16
2.1 Role of precursors ratio	17
2.1.1 Experiment 1 (Indium: Phosphorus – 1:2)	17
2.1.2 Experiment 2 (Indium: Phosphorus – 1:4)	17
2.1.3 Experiment 3 (Indium: Phosphorus – 1:8)	18
2.2 Role of Reaction Time	19
2.2.1 Experiment 4 (Reaction time: 1 hour)	19
2.2.2 Experiment 5 (Reaction time: 2 hours)	19
2.2.3 Experiment 6 (Reaction time: 3 hours)	20

2.3 Reaction temperature	21
2.3.1 Experiment 7 (Reaction temperature: 60 °C)	21
2.3.2 Experiment 8 (Reaction temperature: 80 °C)	21
2.3.3 Experiment 9 (Reaction temperature: 100 °C)	22
2.4 Purification	23
2.5 Characterization	23
2.6 References	24
III. Results and discussion	25
3.1 Role of procure ratio	26
3.2 Role of reaction time	27
3.3 Reaction temperature	29
3.4 Standardized low temperature InP NCs synthesis protocol	31
3.5 References	34
IV. Conclusion	35

Abbreviations

DDA	Dodecylamine
DME	1,2- Dimethoxyethane
en	Ethylenediamine
LED	Light-emitting diode
NCs	Nanocrystals
ODE	1-Octadecene
PL	Photoluminescence
PXRD	Powder X-ray diffractometer
QDs	Quantum dots
QY	Quantum yield
TOP	Trioctylphosphine
TOPO	Trioctylphosphine oxide
TMS	Trimethylsilyl
TEM	Transmission electron microscopy
UV	Ultraviolet
Vis	Visible
W	Wurtzite
ZB	Zinc blende

Symbols

a_B	Bohr radius
$(\text{CH}_3)_3\text{In}$	Trimethyl indium
$[(\text{CH}_3)_3\text{Si}]_3\text{P}$	Tris(trimethylsilyl)phosphine
e^-	Electron
E_g	Band gap energy
$E_g^{(bulk)}$	Band gap energy of bulk material
ϵ_0	Absolute dielectric constants of the medium
ϵ_r	Relative dielectric constants of the medium
h^+	Hole
HCl	Hydrochloric acid
In	Indium
$\text{In}(\text{CH}_3\text{COO})_3$	Indium triacetate
InBr_3	Indium tribromide
InCl_3	Indium trichloride
InP	Indium phosphide
KBH_4	potassium borohydride
LiEt_3BH	Lithium triethylborohydride
m_0	Rest mass of an electron
m_e	Effective mass of an electron
m_h	Effective mass of a hole

nm	Nanometer
NaBH ₄	Sodium borohydride
Na ₃ P	Trisodium phosphide
PBr ₃	Phosphorus tribromide
PCl ₃	Phosphorus trichloride
PH ₃	phosphine gas
P(N(CH ₃) ₂) ₃	Tris(dimethylamino)phosphonine

Chapter I

Introduction

1.1 Introduction:

The term “nano” is derived from the Greek word for “dwarf”, “nanos”[1]. On the metric scale “nano” means “ 10^{-9} ”(e.g. 1 nm= 10^{-9} m). This etymology makes us understand that the tiny dimensions not visible to the naked eye are involved. Colloidal Group 13-Group 15 semiconductor nanocrystals (III-V NCs) also known as quantum dots (QDs) [2] have been the subject of intensive theoretical and experimental study during the last two decades. This is attributed to the rich phenomenon associated with quantum confinement [3, 4] effects that arise when the size of a nanoparticle becomes comparable to or smaller than the effective Bohr radius [5]. The most interesting characteristic of quantum dots (QDs) is the fact that they are band gap-tunable materials by the size [6-8] and as a result their fluorescence characteristics can also be varied. When compared to organic dyes, QDs have several optical merits, such as a narrow, tunable, and symmetric emission spectrum and exceptional photochemical stability. Consequently, QDs have found many applications in, for instance, light-emitting diodes (LEDs) [9-19], photovoltaic devices [20-28] and biolabeling [29-34]. However, extensive adoption of QDs by industry has been severely slowed down because they are highly toxic and pose a potential threat to the environment [35, 36].

1.2 Quantum Dots (QDs)

1.2.1 Definition

Quantum dots are semiconductor materials in which electron-hole pairs (*excitons*) are confined in three dimensions. Quantum dots are usually smaller than 10 nm and exhibit relatively monodisperse size distribution [37]. Since physical dimensions of quantum dot's are comparable to the carrier de Broglie wave function in semiconductors, energy states of the electrons and holes are quantized [5]. As a result, the emission efficiencies of the semiconductor QDs are substantially higher than those of their bulk counterparts and most importantly, the emission wavelength varies as a function of size [38]. These properties make QDs very attractive for optical device applications. Furthermore, the “dark” (optically forbidden) character of the lowest

excitonic state [39] and the long carrier lifetimes measured [40] in colloidal dots are characteristics which make QDs good candidates for spintronics and quantum computing applications.

1.2.2 Properties of quantum dots

1.2.2.1 Quantum confinement effect

When an electron is excited from the valence band to the conduction band in a semiconductor, it leaves behind a positively charge vacancy known as hole. In bulk semiconductors, the electron-hole pair (i.e. exciton) is bound within a characteristic length referred to as exciton Bohr radius (a_B), which is given by the equation 1.1 [37]

$$a_B = \frac{4\pi\epsilon_0\epsilon_r\hbar^2}{m_0e^2} \left[\frac{1}{m_{e^*}} + \frac{1}{m_{h^*}} \right] \quad 1.1$$

Where ϵ_0 and ϵ_r are the absolute and relative dielectric constants of the medium respectively, m_0 is the rest mass of an electron, e is the fundamental electric charge, m_{e^*} and m_{h^*} are the effective masses of an electron and hole exciton pair respectively. When the size of the semiconductor particle approaches the exciton Bohr radius, spacial confinement of the electrons and holes occur which results in discrete atomic like energy spectra. In nearly spherical semiconductor NCs i.e. quantum dots, the confinement occurs in all three dimensions. One of the interesting consequences of this discreteness of energy levels is that semiconductor NCs exhibit size dependent electronic and optical properties.

The size dependency of the band gap is the most prominent effect of quantum confinement. The band gap E_g of QDs having diameter a is given by the following equation 1.2 [37]

$$E_g = E_g^{(bulk)} + \frac{3\epsilon_0\epsilon_r\hbar^2\pi^2}{2a^2} \left[\frac{1}{m_{e^*}} + \frac{1}{m_{h^*}} \right] \quad 1.2$$

Where $E_g^{(bulk)}$ is the band gap of the bulk material.

1.2.2.2 Optical properties of semiconductor nanoparticles

1.2.2.2.1 Absorption

The absorption of a photon with energy greater than the band gap excites an electron from the valence band to the conduction band, creating an electron-hole (i.e. exciton)

pair in a direct band gap semiconductor materials. The excitonic state with the lowest energy appears as a peak in an absorption spectrum of the NCs sample. This peak often referred to as first excitonic peak which has an energy slightly lower than the band gap energy of the sample due to the contribution of the coulomb attraction. The band gap is the energy required to create an electron (e^-) and a hole (h^+) at rest with the lattice and far apart enough so that the coulomb attraction is negligible [41]. The excitonic peak position depends on the band gap of the material as well as on the size of the NCs. The increase of the size of the NC leads to the red-shift of the absorption onset. This is attributed to the quantum confinement effect.

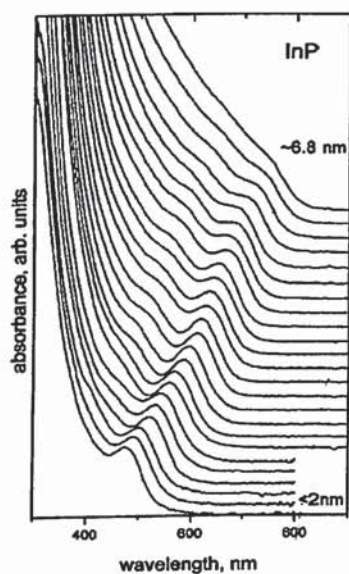


Fig 1.1 Size- dependent evolution of the UV-Vis absorption spectra of InP NCs [42]

1.2.2.2.2 Photoluminescence

Depending upon the electronic configuration of the excited state and emission tract, photoluminescence can be classified into two categories fluorescence and phosphorescence. After the absorption of a photon by the NC which leads to the formation of an exciton, the system can relax to the ground state by radiative recombination of the electron-hole pair. Radiative decay through the emission of

photons is called photoluminescence or more specifically in case of semiconductor QDs fluorescence. The emitted photons have an energy corresponding to the band gap of the NCs and that is why the emission colour can be tuned by changing the particle size [43]. The emission efficiency of QDs is expressed in terms of the fluorescence quantum yield (QY) which is the ratio between the number of photon absorbed and the number of photons emitted. The photoluminescence of NCs at room temperature is often poor due to the surface defects which cause non-radiative desexcitation channels [44].

1.2.2.3 Crystal structure

The most common crystal structures possessed by II-IV and III-V semiconductor NCs are either the cubic zinc blende (ZB) or the hexagonal wurtzite (w). The crystal structures are shown in the figure 1.2[45].Both structures have tetrahedrally coordinated atoms and showing an ABCABC or an ABAB sequence, respectively. Depending on the experimental conditions, nucleation and growth of the NCs can take place in either zinc blende or wurtzite structure and also the coexistence of both the structures in the same nanoparticles is possible [43].

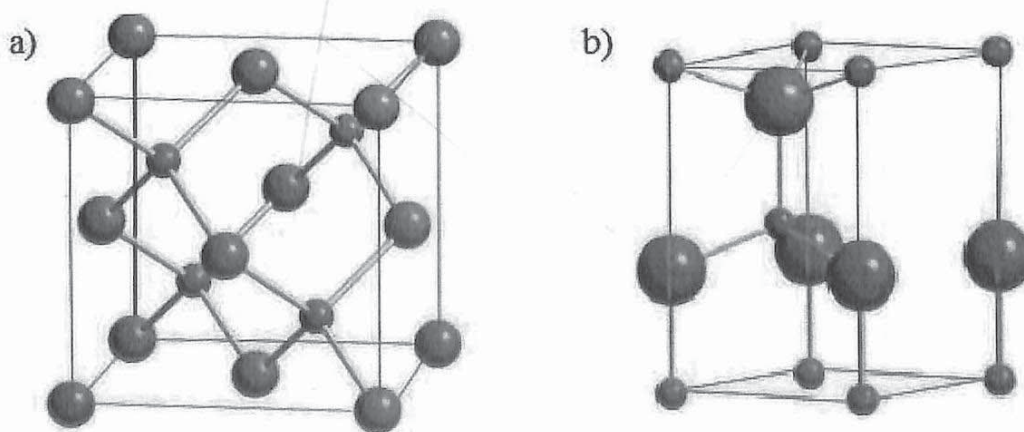


Figure 1.2 a) Zinc blende and b) Wurtzite structure [45]

1.3 Synthesis of indium phosphide (InP) NCs

InP is a low band gap (bulk value: 1.35 eV) III-V semiconductor with an exciton Bohr's radius of 11.5 nm [46]. Various methods have been developed for the synthesis of III-V group materials with nanometer sized dimensions. In the early phase of InP NCs synthesis, strongly coordinating solvent system such as trioctylphosphine oxide (TOPO)/trioctylphosphine (TOP) was commonly chosen [47, 48, 49]. After that, non-coordinating (eg. octadecene) [50, 51] or weakly coordinating solvent (ester) [52] has been newly adopted with a variety of fatty acid ligands, resulting in better quality InP NCs [53].

In the synthesis of high quality InP NCs, a choice of indium (In) precursor is flexible such as $\text{In}(\text{CH}_3\text{COO})_3$, InCl_3 and $(\text{CH}_3)_3\text{In}$, but that of phosphorus precursor is quite limited, mostly relying on a highly expensive, toxic, flammable phosphorus source of tris(trimethylsilyl)phosphine, $\text{P}(\text{TMS})_3$ [53]. It is thus desirable to replace $\text{P}(\text{TMS})_3$ with a greener, cheaper phosphorus precursor [52]. Recently, synthetic efforts to come up to one's expectations on alternative phosphorus sources have been made with white phosphorus (P_4), phosphorus trichloride, PCl_3 and tris(dimethylamino)phosphine, $\text{P}(\text{N}(\text{CH}_3)_2)_3$ via their own synthetic routes [53].

The method of preparation and particle size determine the physical and electronic properties of the semiconductor nanoparticles produced [54]. This gives chemists the unique ability to change the electronic and chemical properties of a semiconductor material by controlling the particle size and preparative conditions employed [54]. However, synthetic studies of III-V semiconductor nanoparticles are much less mastered compared to the II-VI analogues even though they possess a higher degree of covalent bonding, a less ionic lattice and larger exciton diameters resulting in more pronounced quantum size effects in the optical spectra, which are desirable for applications in optical devices [55]. The preparation of well-crystallized QDs of III-V compounds require high temperature [47, 49, 50] and the relevant solution chemistry at low temperature is still not well-developed [56].

1.3.1 High temperature synthesis route:

The majority of the existing routes for the synthesis of InP colloidal nanocrystals (NCs) found in literature are based on Well's dehalosilylation reaction [57] first adapted by Micic *et. al.* [58] for colloidal InP NCs. In this reaction tris(trimethylsilyl)phosphine, $[(\text{CH}_3)_3\text{Si}]_3\text{P}$ is reacted with an indium (III) precursor at elevated temperatures (180 °C-300 °C) in a high boiling solvent and invariably in presence of a stabilising ligand (e.g. fatty acids [59], amines [60, 61] and/or the alkyl phosphine [62]). Larger sized NCs are typically synthesised *via* multiple injections of precursor solutions to the solution of smaller InP NCs at high temperatures [46, 60], often followed by a size selective precipitation step [46]. The longest emission reported for InP NCs by this method is ~750 nm [46, 60]. Based on afore mentioned Well's dehalosilylation reaction Alivisatos *et. al.* have prepared a series of III-V semiconductors as shown below [63]:



In 2002, Talapin *et. al.* prepared InP nanocrystals by an organometallic synthesis using mixtures of highly boiling primary amines and trioctylphosphine (TOP) as the coordinating solvent [64]. They used amines to obtain small crystalline InP nanoparticles. InP nanocrystals with the mean particle size in the range of 1.5 – 4.0 nm possess a weak emission (< 1% quantum efficiency) [64]. For the above reaction to take place they maintained the temperature in the range of 150 °C - 240 °C. In this publication, they used anhydrous InCl_3 , $(\text{TMS})_3\text{P}$ in TOP along with dodecylamine (DDA) as a stabilizing agent [64].

In the same year, Battaglia and Peng reported the formation of high quality InP nanocrystals in a noncoordinating solvent [59]. Within the experimental conditions explored, fatty acids with well-defined chain lengths, a noncoordinating solvent, a

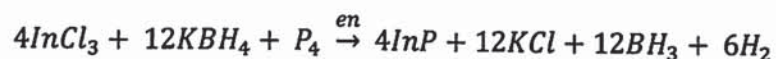
well-controlled indium-to-ligand ratio and a thorough degassing process are all critical factors for a successful synthesis of InP nanocrystals with an acceptable quality without any size sorting [59]. In this publication, octadecene (ODE) was used as the noncoordinating solvent [59]. Indium acetate, $\text{In}(\text{CH}_3\text{COO})_3$ and tris(trimethylsilyl)phosphine, $\text{P}(\text{TMS})_3$ were used as the indium and phosphorus precursors respectively. The best results were achieved by maintaining a 2:1 indium to phosphorus molar ratio and the temperature range was 250 °C-300 °C [59]. Acetone and methanol were used to precipitate the nanocrystals in order to remove starting materials and side products [59]. PXRD and TEM measurements were performed to characterize the crystallinity, size and size distribution of the resulting crystals [59].

Another way of synthesising InP NCs is using phosphine gas as the phosphorous precursor [65]. In this method, the *in situ* generated phosphine gas is reacted with the indium precursor in the presence of a ligand at high temperature (210 °C to 290 °C). Since the PH_3 gas is slowly and continuously bubbled into the flask containing the precursor solutions, similar to the aforementioned multiple injection method, the overall size is expected to be larger. Qian et al. used the solvothermal method to prepare nanocrystalline InP of the size 12 nm by using InCl_3 as the indium precursor and Na_3P as the phosphorus precursor in presence of the coordinating solvent 1,2-dimethoxyethane (DME) at a temperature of 180 °C for 12 hrs [66].

1.3.2 Low temperature synthesis route:

Despite of successes in the synthesis of InP nanocrystals, most methods involve high reaction temperature and pyrophoric phosphorus precursor. The need to develop low temperature synthesis methods have been addressed by some recent publications [67, 68, 69]. For example, in 1999, Qian and co-workers reported synthesis of InP nanocrystals at temperatures as low as 80 °C [70]. In this publication, they have used KBH_4 as a reducing agent to reduce metal salts in organic solvents like

ethylenediamine (en). The precursors they have used are InCl_3 and yellow phosphorus and the given pathway is as follows [70]:



From X-ray powder diffraction, mean crystalline dimensions of 11.3-20 nm InP were determined [70]. When prepared at temperature 120 °C, 15-20 nm sized InP spherical grains were obtained which was revealed by transmission electron microscopy [70]. In another publication, Sun *et. al.* have reported a rapid and low temperature method of preparation of InP nanocrystals [71]. The reaction temperature range was 80 °C- 120 °C and the reaction time was less than 2 hours. The precursors they have used are dehydrated InCl_3 and red phosphorus in presence of hexadecane as a solvent and lithium triethylborohydride (LiEt_3BH) as a reducing agent [71]. From transmission electron microscopic (TEM) image, the average particle size of InP was estimated as ~5.5 nm [71]. In the year 2008, Peter Reiss and his group published a paper on “low temperature synthesis of InP nanocrystals” [72]. In this report they have synthesized InP NCs by using $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ and yellow phosphorus as the indium and phosphorus precursors, respectively and NaBH_4 as the reducing agent in a ultrasound-assisted reaction in presence of mixed solvent of ethanol and toluene [72]. The reaction temperature was less than 75 °C and the reaction time was in between 1-5 h. From powder X-ray diffraction and Raman scattering measurements, the structure of InP NCs was confirmed to be in the zinc-blende form [72]. The average particle size of 4 nm had been determined by transmission electron microscopic (TEM) image, Raman scattering and absorption spectroscopy [72]. On the other hand, for the first time, Gao *et. al.* have reported mild aqueous synthesis of crystalline and monodisperse InP and GaP nanocrystals [69]. The reaction was carried out at a temperature range of 120 °C- 160 °C and the average crystallite sizes of InP estimated by the Scherrer equation was about 8 nm [69].

Although a few low temperature synthesis methods have been reported [69-72] yet, the

low temperature synthesis of InP or any other III-V semiconductor still remains an attractive research problem in view of crystallinity, monodispersity and quantum yield compared to ones prepared at higher temperatures using toxic tris(trimethylsilyl)phosphine (P(TMS)₃) [59] or Phosphine gas [65] as phosphorous precursor.

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Chapter II

Materials and Methodology

2.1. Role of precursors ratio

2.1.1. Experiment 1 (Indium: Phosphorous - 1:2)

At first, InBr_3 (0.25 mmol, $\sim 0.0898\text{g}$; 99%, Aldrich) was dissolved in 1 mL acetonitrile (99.5%, Merck) in a sample vial at room temperature. (**Comment:** We have chosen acetonitrile (CH_3CN) as a solvent for dissolving InBr_3 because it is highly soluble in acetonitrile at room temperature). In a measuring flask, 0.2 M NaBH_4 (5 mmol, 0.1897 g dissolved in 25 mL ethylenediamine) solution was prepared. (**Comment:** we have chosen NaBH_4 as a reducing agent for following reasons: One, it is soluble in ethylenediamine at room temperature. Two, its large commercial availability and low price as compared to its homologue potassium (i.e. potassium borohydride, KBH_4) [1]. Here the role of NaBH_4 is to reduce InBr_3 to generate active atomic In and *in situ* generation of PH_3 gas [2]). Separately, in a two neck round bottom flask, 10 mL ethylenediamine (99%, Merck) was taken and heated to 60 °C. (**Comment:** We have chosen ethylenediamine as the reaction solvent as it has a boiling point of 117.42 °C which is not so high.) To it InBr_3 solution was added. At the time of addition of InBr_3 solution to ethylenediamine white turbidity appeared. After that PBr_3 (0.5 mmol, $\sim 50\ \mu\text{L}$; 99%, Aldrich) was added. To the resulting mixture 0.2 M NaBH_4 (96%, Thomas Baker) solution was added drop wise (it takes ~ 15 min). The resulting reaction mixture was heated at 100 °C for 3 hours. At the time of addition of InBr_3 and PBr_3 , the colour of the reaction mixture was brownish. After 1 hour, the resulting mixture became black in colour. The reaction mixture was allowed to cool to room temperature normally.

After that the reaction mixture was treated with 7 mL 2 M HCl (35%, Merck) solution and heated the reaction mixture to 100 °C for 1 hour. The most crucial step for the purification is the washing with dilute HCl solution. PXRD spectra was taken.

2.1.2. Experiment 2 (Indium : Phosphorous - 1:4)

At first, InBr_3 (0.25 mmol, $\sim 0.0898\ \text{g}$; 99%, Aldrich) was dissolved in 1 mL acetonitrile (99.5%, Merck) in a sample vial at room temperature. In a measuring flask, 0.2 M NaBH_4 (5 mmol, 0.1897 g dissolved in 25 mL ethylenediamine) solution

was prepared. Separately, in a two neck round bottom flask, 10 mL ethylenediamine (99%, Merck) was taken and heated to 60 °C. To it InBr_3 solution was added. At the time of addition of InBr_3 solution to ethylenediamine white turbidity appeared. After that PBr_3 (1.0 mmol, ~100 μL ; 99%, Aldrich) was added. To the resulting mixture 0.2 M NaBH_4 (96%, Thomas Baker) solution was added drop wise (it takes ~15 min). The resulting reaction mixture was heated at a temperature of 100 °C for 3 hours. At the time of addition of InBr_3 and PBr_3 , the colour of the reaction mixture was brownish. After 1 hour, the resulting mixture became black in colour. The reaction mixture was allowed to cool to room temperature normally.

After that the reaction mixture was treated with 7 mL 2 M HCl (35%, Merck) solution and heated the reaction mixture to 100 °C for 1 hour. The most crucial step for the purification is the washing with dilute HCl solution. PXRD spectra was taken.

2.1.3. Experiment 3 (Indium : Phosphorous - 1:8)

At first, InBr_3 (0.25 mmol, ~ 0.0898 g; 99%, Aldrich) was dissolved in 1 mL acetonitrile (99.5%, Merck) in a sample vial at room temperature. In a measuring flask, 0.2 M NaBH_4 (5 mmol, 0.1897 g dissolved in 25 mL ethylenediamine) solution was prepared. Separately, in a two neck round bottom flask, 10 mL ethylenediamine (99%, Merck) was taken and heated to 60 °C. To it InBr_3 solution was added. At the time of addition of InBr_3 solution to ethylenediamine white turbidity appeared. After that PBr_3 (2.0 mmol, ~200 μL ; 99%, Aldrich) was added. To the resulting mixture 0.2 M NaBH_4 (96%, Thomas Baker) solution was added drop wise (it takes ~15 min). The resulting reaction mixture was heated at a temperature of 100 °C for 3 hours. At the time of addition of InBr_3 and PBr_3 , the colour of the reaction mixture was brownish. After 1 hour, the resulting mixture became black in colour. The reaction mixture was allowed to cool to room temperature normally.

After that the reaction mixture was treated with 7 mL 2 M HCl (35%, Merck) solution and heated the reaction mixture to 100 °C for 1 hour. The most crucial step for the

purification is the washing with dilute HCl solution. PXRD, UV-Vis, PL and TEM image was taken.

2.2 Role of reaction time:

2.2.1 Experiment 4 (Reaction time: 1 hour)

At first, InBr_3 (0.25 mmol, ~ 0.0898 g; 99%, Aldrich) was dissolved in 1 mL acetonitrile (99.5%, Merck) in a sample vial at room temperature. In a measuring flask, 0.2 M NaBH_4 (5 mmol, 0.1897 g dissolved in 25 mL ethylenediamine) solution was prepared. Separately, in a two neck round bottom flask, 10 mL ethylenediamine (99%, Merck) was taken and heated to 60 °C. To it InBr_3 solution was added. At the time of addition of InBr_3 solution to ethylenediamine white turbidity appeared. After that PBr_3 (2.0 mmol, ~200 μL ; 99%, Aldrich) was added. To the resulting mixture 0.2 M NaBH_4 (96%, Thomas Baker) solution was added drop wise (it takes ~15 min). The resulting reaction mixture was heated at a temperature of 100 °C for 1 hour. At the time of addition of InBr_3 and PBr_3 , the colour of the reaction mixture was brownish. After 1 hour, the resulting mixture became black in colour. The reaction mixture was allowed to cool to room temperature normally.

After that the reaction mixture was treated with 7 mL 2 M HCl (35%, Merck) solution and heated the reaction mixture to 100 °C for 1 hour. The most crucial step for the purification is the washing with dilute HCl solution. PXRD spectra was taken before and after treatment with HCl. UV-Vis and PL spectra was taken.

2.2.2 Experiment 5 (Reaction time: 2 hours)

InBr_3 (0.25 mmol, ~ 0.0898 g; 99%, Aldrich) was dissolved in 1 mL acetonitrile (99.5%, Merck) in a sample vial at room temperature. In a measuring flask, 0.2 M NaBH_4 (5 mmol, 0.1897 g dissolved in 25 mL ethylenediamine) solution was prepared. Separately, in a two neck round bottom flask, 10 mL ethylenediamine (99%, Merck) was taken and heated to 60 °C. To it InBr_3 solution was added. At the time of

addition of InBr_3 solution to ethylenediamine white turbidity appeared. After that PBr_3 (2.0 mmol, $\sim 200 \mu\text{L}$; 99%, Aldrich) was added. To the resulting mixture 0.2 M NaBH_4 (96%, Thomas Baker) solution was added drop wise (it takes ~ 15 min). The resulting reaction mixture was heated at a temperature of $100 \text{ }^\circ\text{C}$ for 2 hours. At the time of addition of InBr_3 and PBr_3 , the colour of the reaction mixture was brownish. After 1 hour, the resulting mixture became black in colour. The reaction mixture was allowed to cool to room temperature normally.

After that the reaction mixture was treated with 7 mL 2 M HCl (35%, Merck) solution and heated the reaction mixture to $100 \text{ }^\circ\text{C}$ for 1 hour. The most crucial step for the purification is the washing with dilute HCl solution. PXRD spectra was taken before and after treatment with HCl. UV-Vis and PL spectra was taken.

2.2.3 Experiment 6 (Reaction time: 3 hours)

At first, InBr_3 (0.25 mmol, ~ 0.0898 g; 99%, Aldrich) was dissolved in 1 mL acetonitrile (99.5%, Merck) in a sample vial at room temperature. In a measuring flask, 0.2 M NaBH_4 (5mmol, 0.1897 g dissolved in 25 mL ethylenediamine) solution was prepared Separately, in a two neck round bottom flask, 10 mL ethylenediamine (99%, Merck) was taken and heated to $60 \text{ }^\circ\text{C}$. To it InBr_3 solution was added. At the time of addition of InBr_3 solution to ethylenediamine white turbidity appeared. After that PBr_3 (2.0 mmol, $\sim 200 \mu\text{L}$; 99%, Aldrich) was added. To the resulting mixture 0.2 M NaBH_4 (96%, Thomas Baker) solution was added drop wise (it takes ~ 15 min). The resulting reaction mixture was heated at a temperature of $100 \text{ }^\circ\text{C}$ for 3 hours. At the time of addition of InBr_3 and PBr_3 , the colour of the reaction mixture was brownish. After 1 hour, the resulting mixture became black in colour. The reaction mixture was allowed to cool to room temperature normally.

After that the reaction mixture was treated with 7 mL 2 M HCl (35%, Merck) solution and heated the reaction mixture to $100 \text{ }^\circ\text{C}$ for 1 hour. The most crucial step for the purification is the washing with dilute HCl solution. PXRD, UV-Vis, PL and TEM image was taken.

2.3 Reaction temperature

2.3.1 Experiment 7 (Reaction temperature: 60 °C)

At first, InBr_3 (0.25 mmol, ~ 0.0898 g; 99%, Aldrich) was dissolved in 1 mL acetonitrile (99.5%, Merck) in a sample vial at room temperature. In a measuring flask, 0.2 M NaBH_4 (5 mmol, 0.1897 g dissolved in 25 mL ethylenediamine) solution was prepared. Separately, in a two neck round bottom flask, 10 mL ethylenediamine (99%, Merck) was taken and heated to 60 °C. To it InBr_3 solution was added. At the time of addition of InBr_3 solution to ethylenediamine white turbidity appeared. After that PBr_3 (2.0 mmol, ~200 μL ; 99%, Aldrich) was added. To the resulting mixture 0.2 M NaBH_4 (96%, Thomas Baker) solution was added drop wise (it takes ~15 min). The resulting reaction mixture was heated at a temperature of 60 °C for 3 hours. At the time of addition of InBr_3 and PBr_3 , the colour of the reaction mixture was brownish. After 1 hour, the resulting mixture became black in colour. The reaction mixture was allowed to cool to room temperature normally.

After that the reaction mixture was treated with 7 mL 2 M HCl (35%, Merck) solution and heated the reaction mixture to 60 °C for 1 hour. The most crucial step for the purification is the washing with dilute HCl solution. PXRD spectra was taken before and after treatment with HCl.

2.3.2 Experiment 8 (Reaction temperature: 80 °C)

InBr_3 (0.25 mmol, ~ 0.0898 g; 99%, Aldrich) was dissolved in 1 mL acetonitrile (99.5%, Merck) in a sample vial at room temperature. In a measuring flask, 0.2 M NaBH_4 (5 mmol, 0.1897 g dissolved in 25 mL ethylenediamine) solution was prepared. Separately, in a two neck round bottom flask, 10 mL ethylenediamine (99%, Merck) was taken and heated to 60 °C. To it InBr_3 solution was added. At the time of addition of InBr_3 solution to ethylenediamine white turbidity appeared. After that PBr_3 (2.0 mmol, ~200 μL ; 99%, Aldrich) was added. To the resulting mixture 0.2 M NaBH_4 (96%, Thomas Baker) solution was added drop wise (it takes ~15 min). The resulting reaction mixture was heated at a temperature of 80 °C for 3 hours. At the

time of addition of InBr_3 and PBr_3 , the colour of the reaction mixture was brownish. After 1 hour, the resulting mixture became black in colour. The reaction mixture was allowed to cool to room temperature normally.

After that the reaction mixture was treated with 7 mL 2 M HCl (35%, Merck) solution and heated the reaction mixture to 80 °C for 1 hour. The most crucial step for the purification is the washing with dilute HCl solution. PXRD spectra was taken before and after treatment with HCl.

2.3.3 Experiment 9 (Reaction temperature: 100 °C)

InBr_3 (0.25 mmol, ~ 0.0898 g; 99%, Aldrich) was dissolved in 1 mL acetonitrile (99.5%, Merck) in a sample vial at room temperature. In a measuring flask, 0.2 M NaBH_4 (5 mmol, 0.1897 g dissolved in 25 mL ethylenediamine) solution was prepared. Separately, in a two neck round bottom flask, 10 mL ethylenediamine (99%, Merck) was taken and heated to 60 °C. To it InBr_3 solution was added. At the time of addition of InBr_3 solution to ethylenediamine white turbidity appeared. After that PBr_3 (2.0 mmol, ~200 μL ; 99%, Aldrich) was added. To the resulting mixture 0.2 M NaBH_4 (96%, Thomas Baker) solution was added drop wise (it takes ~15 min). The resulting reaction mixture was heated at a temperature of 100 °C for 3 hours. At the time of addition of InBr_3 and PBr_3 , the colour of the reaction mixture was brownish. After 1 hour, the resulting mixture became black in colour. The reaction mixture was allowed to cool to room temperature normally.

After that the reaction mixture was treated with 7 mL 2 M HCl (35%, Merck) solution and heated the reaction mixture to 100 °C for 1 hour. The most crucial step for the purification is the washing with dilute HCl solution. PXRD spectra was taken before and after treatment with HCl.

2.4 Purification: To about 3 ml as synthesized InP nanocrystals solution, 4 mL ethanol water (1:2) mixture was added and centrifuged at 6000 rpm for 3 minutes. The pellet was collected and the procedure was repeated 3-4 times. The pellet was vacuum dried for about 30 minutes at room temperature. Finally the dry pellet was dispersed in chloroform for characterization.

2.5 Characterization: UV-Vis and PL spectra were obtained with dilute InP nanocrystals solution in chloroform (99.0-99.4%, Merck). Measurements were performed with Perkin Elmer Lambda25 UV-Vis spectrometer. The same dilute solution was used for taking fluorescence spectra with Perkin Elmer LS 55 Fluorescence Spectrometer. For the structural characterization of the samples powder X-ray diffraction (PANalytical, X'Pert PRO) was performed. High-resolution transmission electron microscopy (HRTEM JEM-2100) enabled us to determine directly the NCs' size and shape.

2.6 References:

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Chapter III

Results and Discussion

3.1 Role of precursors ratio

Multiple experiments were performed using different In: P precursor ratio. Other reaction conditions such as temperature, time and solvent volume were kept unchanged. The as-synthesized products were treated with same amount of HCl in all cases and PXRD spectra were obtained for comparisons. It was evident from the PXRD studies that the synthesis of In-atom-free InP nanocrystals is possible using higher amount of phosphorus precursor. Figure 3.1a shows the comparative PXRD spectra of InP nanocrystals obtained using three different In: P ratios 1:8, 1:4 and 1:2. When lower amount of phosphorous precursors were used, Indium impurities were detected in the product even after the HCl treatment. This also indicates the suggested mechanism of InP formation i.e., *via* reaction between in-situ generated atomic In and PH_3 gas. Presence of non-polar P-H bonds in PH_3 could be the reason for its poor solubility in the solvent we use (ethylenediamine, which is polar), hence poor reactivity with In.

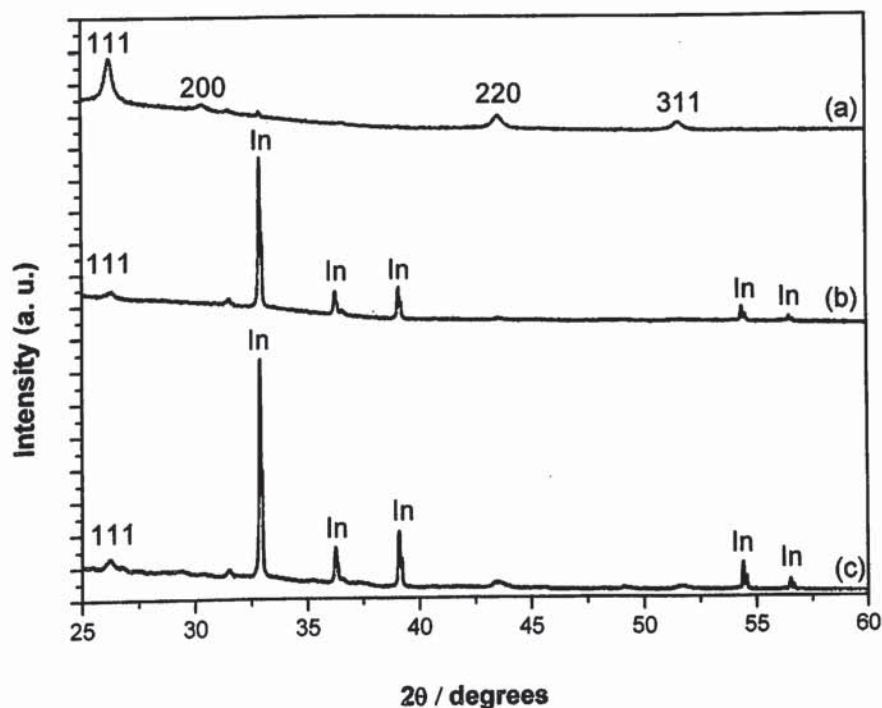


Fig 3.1a: PXRD patterns of the InP prepared by using the In: P ratio (a) 1:8; (b) 1:4; (c) 1:2

3.2 Role of reaction time:

To optimize the reaction time, syntheses of InP nanocrystals were carried out at 1 hour, 2 hours and 3 hours and results were analyzed with UV-Vis, PL and PXRD study. In these three sets of experiments precursor ratio was kept at 1:8 and temperature was kept at 100 °C. The as-synthesized products were treated with same amount of HCl in all cases. It was evident from the UV-Vis absorption (Fig. 3.2a) studies that as we increase the reaction time from 1 hour to 3 hours via 2 hours the characteristic first excitonic peak of InP NC becomes more prominent indicative of better size distribution. Also, the first excitonic peak is red shifted as the reaction time is prolonged. Figure 3.2a also shows the corresponding PL spectra of InP. The quantum yield of the InP nanocrystal is very low as expected of pure InP nanocrystals without surface passivation or etching with HF [1-4].

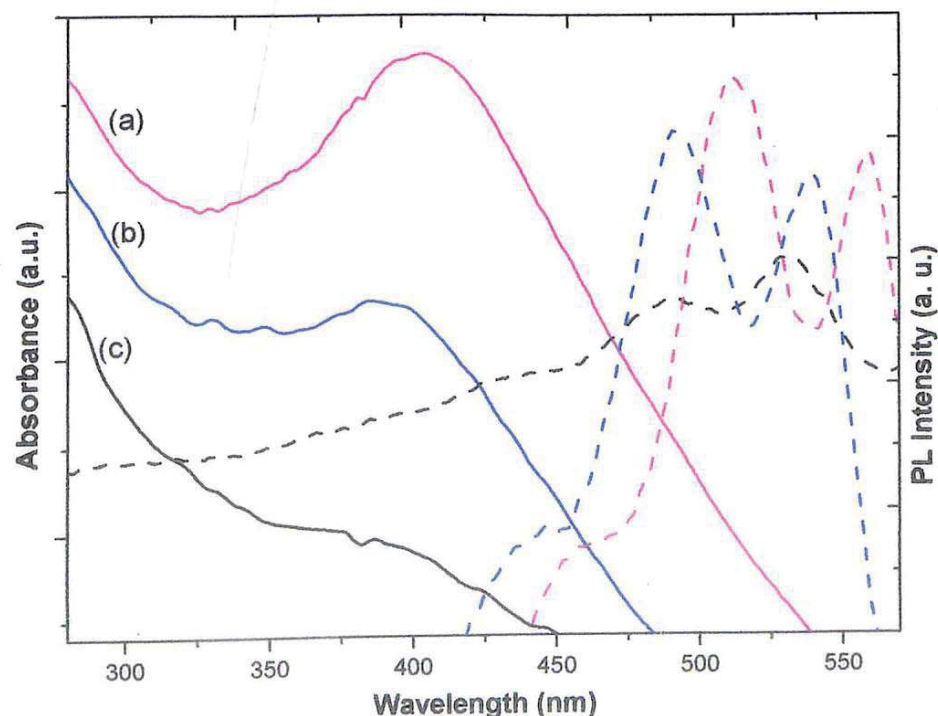


Fig 3.2a: UV-Vis vs PL spectra of InP prepared at 100°C with different time scale viz. (a) pink-3 hours (b) blue- 2 hours and (c)black- 1 hour.

Figure 3.2b shows the comparative PXRD spectra of InP nanocrystals obtained at three different temperatures 1 hour, 2 hours and 3 hours. When lower reaction times were used, Indium impurities were detected in the product even after the HCl treatment.

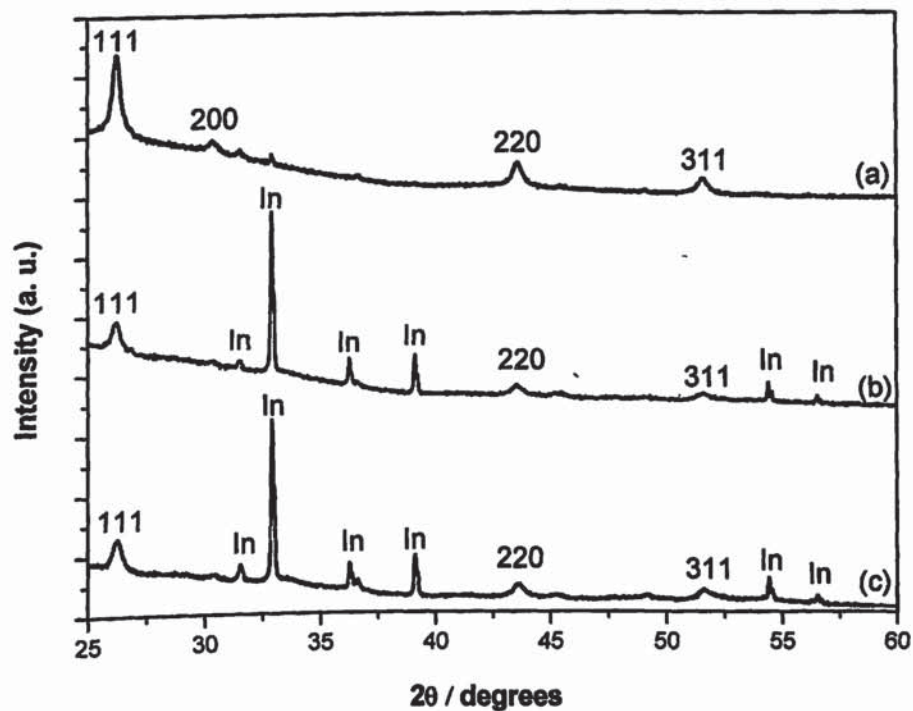


Fig 3.2b: PXRD pattern of the InP prepared at different time scale: (a) 3 hours (b) 2 hours and (c) 1 hour.

3.3 Reaction temperature

The reaction temperature is a crucial factor in the process of synthesis of InP NCs. The syntheses of InP nanocrystals were carried out at 60 °C, 80 °C and 100 °C and results were analyzed with PXRD study. In these three sets of experiments precursor ratio was kept at 1:8 and time was kept at 3 hours. The as-synthesized products were treated with same amount of HCl in all cases. Although with the method described here we were able to synthesise InP nanocrystals at temperature as low as 60 °C however, some In impurities were also detected in PXRD. Figure 3.3a shows the comparative PXRD spectra of InP nanocrystals obtained using three different temperatures 60 °C, 80 °C and 100 °C. The relative intensity of the peaks in the PXRD spectra showed that the indium content decreased with reaction temperature.

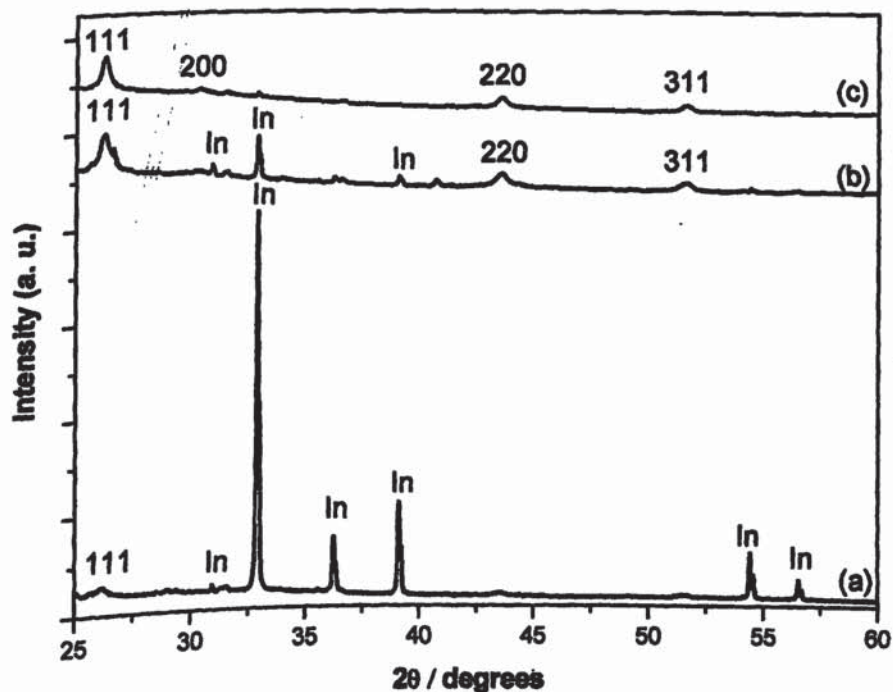


Fig 3.3a: PXRD pattern of the InP prepared at different temperatures: (a) 60 °C (b) 80 °C and (c) 100 °C.

3.3 Reaction temperature

The reaction temperature is a crucial factor in the process of synthesis of InP NCs. The syntheses of InP nanocrystals were carried out at 60 °C, 80 °C and 100 °C and results were analyzed with PXRD study. In these three sets of experiments precursor ratio was kept at 1:8 and time was kept at 3 hours. The as-synthesized products were treated with same amount of HCl in all cases. Although with the method described here we were able to synthesise InP nanocrystals at temperature as low as 60 °C however, some In impurities were also detected in PXRD. Figure 3.3a shows the comparative PXRD spectra of InP nanocrystals obtained using three different temperatures 60 °C, 80 °C and 100 °C. The relative intensity of the peaks in the PXRD spectra showed that the indium content decreased with reaction temperature.

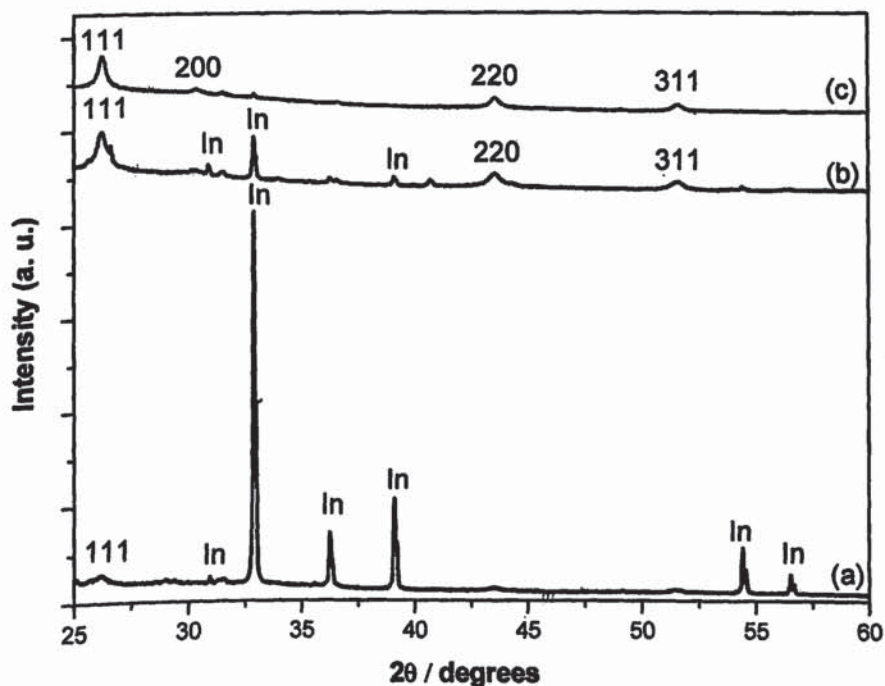
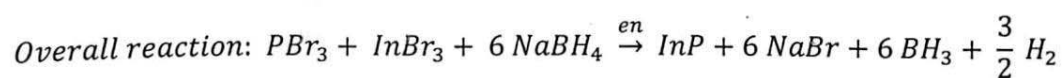
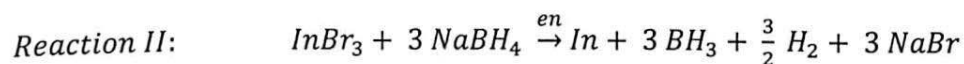
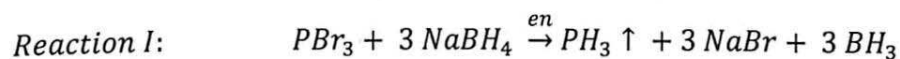


Fig 3.3a: PXRD pattern of the InP prepared at different temperatures: (a) 60 °C (b) 80 °C and (c) 100 °C.

At 100 °C, pure InP was obtained after the HCl treatment. At 60 °C and 80 °C, along with InP, small amount of Indium impurity was also detected even after the HCl treatment. At higher temperature, In and P precursors overcome the activation energy barrier to form stable InP nanocrystals. The plausible reaction mechanism for the preparation of InP is as shown below:



To verify if the Phosphine gas (PH_3) is generated in *Reaction I* we trapped the gas in saturated copper sulphate solution. The blue colour of copper sulphate solution turned to black colour indicative of Cu_3P_2 formation.

In *Reaction II* the formation of active atomic indium (In) takes place which combined with *in situ* generated phosphine gas (*Reaction I*) to form indium phosphide (InP).



The generation of active atomic In from In (III) salt in the presence of a reducing agent has been reported in earlier publications [5].

3.4 Standardized low temperature InP NCs synthesis protocol:

Based on above experiments the optimum condition for the synthesis of *pure* InP nanocrystals-without any In impurities-is as follows:

Reaction temperature, 100 °C; Reaction time, 3 hours; and In:P precursor ratio, 1:8. The other experimental details are provided in the experimental section. Figure 3.4a is the PXRD pattern of the pure InP nanocrystals obtained as above. The UV-Vis vs. PL and digital images of the colloidal solution and TEM images of the same sample are provided in the figures 3.4b, 3.4c respectively.

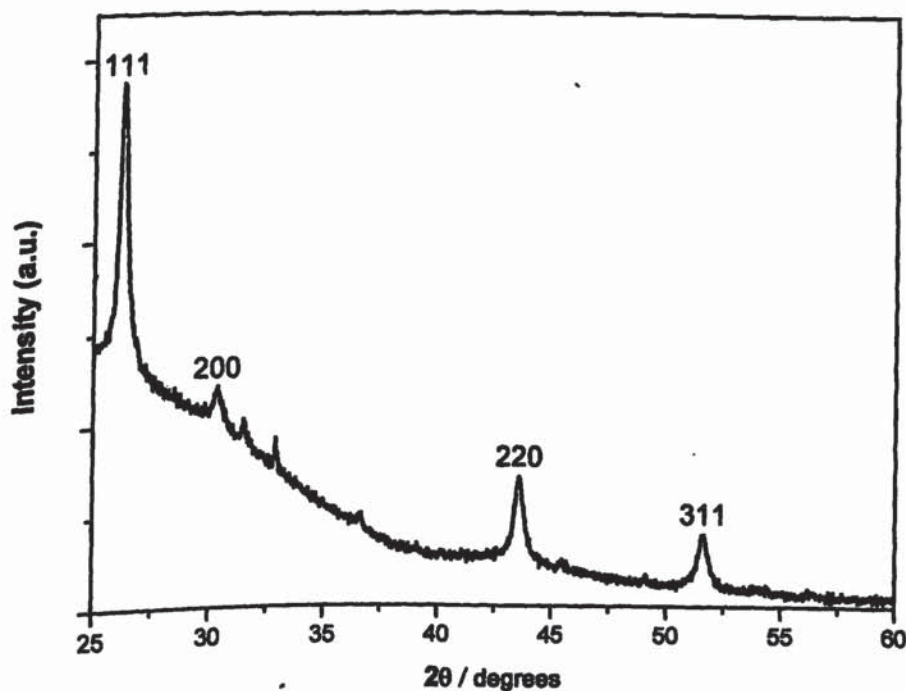


Fig 3.4a: PXRD pattern of the InP prepared with reaction time of 3 hours. Here the heating temperature was maintained at 100 °C and ratio In:P at 1:8.

The first excitonic peak of the standardised InP nanocrystals sample appeared at 410 nm. This corresponds to the size of about 2 nm. The calculation of the size of the particle from UV-Vis spectroscopy is available in the literature [6]. Briefly, according to Beer's Lambert law, the expression for optical density or absorbance (A) is as follows:

$$A = \log_{10}(I_0/I)$$

where I_0 is the intensity of the light at a given wavelength λ before it enters the sample and I is the intensity of light that has passed through a sample (transmitted intensity). Further,

$$c = \frac{A}{\epsilon \times l}$$

where ϵ is molar extinction coefficient and l is the path length (cm) of the sample (cuvette)

For colloidal semiconductor NCs the molar extinction coefficient in the equation is a size dependent variable. For example, the ϵ of InP quantum dots is given by

$$\epsilon = 3046.1(D)^3 - 76532(D)^2 + (5.5137 \times 10^5)(D) - (8.9839 \times 10^5)$$

where D is the diameter (nm) of the NCs. D can be obtained either directly from TEM micrographs or by measuring the first excitonic peak (λ) in the UV-VIS spectrum. The relation between the first excitonic peak and the diameter is given by the following equation [6]

$$D = (-3.7707 \times 10^{-12})\lambda^5 + (1.0262 \times 10^{-8})\lambda^4 - (1.0781 \times 10^{-5})\lambda^3 + (5.4550 \times 10^{-3})\lambda^2 - (1.3122)\lambda + 119.9$$

The small size (~ 2 nm) of the nanocrystals is also confirmed by the corresponding PL spectra where the band edge emission appears in the range 450-560 nm [Fig. 3.4b]. The HRTEM images show aggregates of the nanoparticles. It may be noted that no stabilizing agent has been used in this synthetic protocol. Moreover, the samples have been rigorously purified prior to TEM analysis [See, section: 2.4]. Lattice fringes with d-spacing of 0.32 nm arising from zinc blende (111) InP crystal planes are clearly observable in high resolution. TEM images and SAED images indicate the high crystalline nature of the particles [Fig. 3.4b]. The crystallite size obtained using Scherrer formula [7] is about 0.5 nm which is smaller than the particle size predicted by UV-Vis spectroscopy. The Scherrer formula provides a lower bound on the crystallite size due to contribution of other factors (e.g. inhomogeneous strain and instrumental effects) to the width of a diffraction peak besides crystallite size [7].

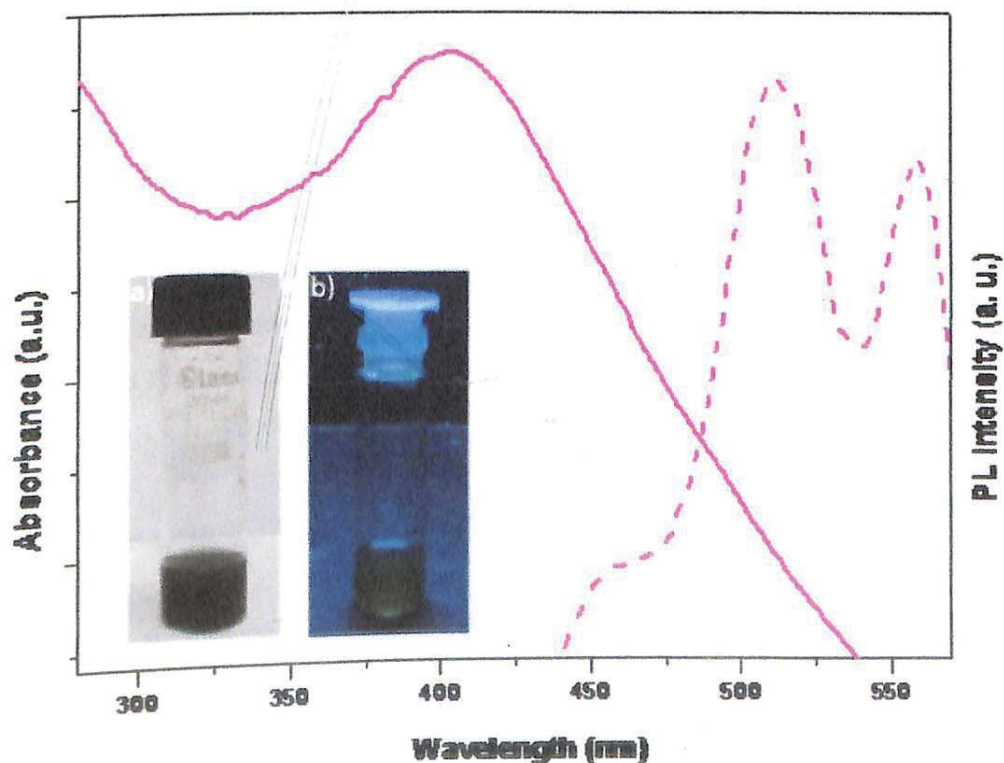


Fig 3.4b: UV-Vis (left) and PL spectra (right) of InP (Excitation: 380 nm). Inset is the digital images of a) colloidal solution of InP in CHCl_3 b) solution of InP under UV lamp.

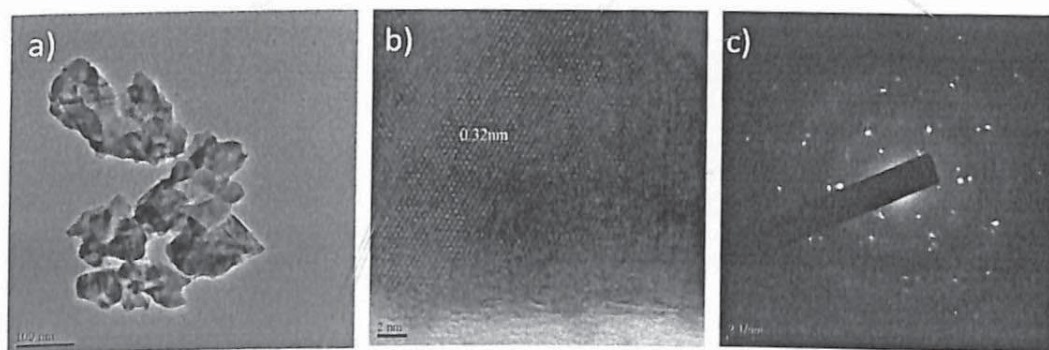


Fig 3.4c: a) TEM image of InP. Here the bar indicates 100 nm. b) HRTEM image of InP. c) Selected area electron diffraction (SAED) image of InP.

3.5 References:

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Chapter IV

Conclusion

We have investigated a low temperature synthetic route for the synthesis of InP NCs. The role of NaBH_4 as a reducing agent is very important in lowering the reaction temperature. It reduces InBr_3 to active atomic In and occasions the *in situ* generation of PH_3 gas. The active In and PH_3 gas reacts in situ to give high crystalline InP nanocrystals at low temperature ($100\text{ }^\circ\text{C}$). The reaction condition has been optimized by changing the reaction parameters such as temperature, precursors ratio and reaction time. The optimized reaction conditions includes In:P precursor ratio, 1:8; reaction temperature, $100\text{ }^\circ\text{C}$ and reaction time of 3 hours without using any inert atmosphere during the reaction. Their surface is not stabilized by surfactant molecules having bulky organic moieties, in contrast to nanoparticles synthesized through traditional colloid-chemical methods. These small ($\sim 2\text{ nm}$), highly crystalline NCs without any lengthy insulating surfactant molecules around them is expected to be useful in photovoltaic applications.