# CHAPTER 2

## Synthesis and Characterization of Indium Arsenide (InAs)

InAs is not a new material. For a long time, it has been known for its promising properties including narrow direct band gap (0.42 eV),[1] and tiny effective mass for electrons and holes ($0.023m_0$ and $0.42m_0$, $m_0$ = free electron mass, respectively)[2] that can be excellently utilized and advanced in various electronics and optoelectronics. Its exciton Bohr radius is also large (~34 nm),[2] which can facilitate the fabrication technology to produce quantum confined particle for specific purposes as well as advance applications. However, arsenic is highly toxic in any forms and causes a drawback in the synthesis process, especially for nanoparticle fabrication. The development has been dealt with this problem by either finding new safer precursors or new safer strategies. To date, InAs NCs are generally synthesized using harmful organometallic compounds as precursors with extreme air-free reaction conditions. When it seems impossible to find new As source that is safe, effective, and also cheap at the same time, we attempt to develop the safe system described in previous work[3] to gain more benefits.

The first half of this chapter shows the experiment details that aim to investigate the hydrothermal effect and reproducible synthesis of a potentially useful InAs nanoparticle. Physical parameters in reaction conditions were studied carefully to understand the reaction behavior and to design a proper system for MW synthesis of InAs nanophase. The experiment section of InAs nanoparticle involves the synthesis procedures using conventional hydrothermal technique and MW-assisted hydrothermal protocol, The latter parts of this chapter describe the investigation of reaction mechanism and characteristic properties. The discussions are also included.

## 2.1 Experiment Methods

**Chemicals**: Indium chloride ($InCl_3$, 99.9%, Sigma-Alrich), Arsenic trioxide ($As_2O_3$, 99.9%, Sigma-Alrich), Zinc powder (Zn, 98%, Acros), Hydrochloric acid (HCl, 37%, RCI Labscan), Nitric acid ($HNO_3$, 70%, J. T. Baker), and all other common reagent-grade chemicals were obtained from RCI Labscan and Qrec. All chemicals were used as received without further purification.

**Equipments**: 200 mL Teflon-lined stainless steel autoclave, 180 mL Modified glass vessel autoclave with built in pressure gauge, Roof-perforated household microwave oven (8 cm hole diameter, Electrolux EMM2009W), Vacuum pump (Sparmax TC-501V), and other common laboratory equipments and glasswares.

**Synthesis Procedures**: InAs nanoparticles were synthesized via a hydrothermal method and all processes should be operated in safety hood. 1 mmol of $InCl_3$ and 2.5 mmol of $As_2O_3$ (1:2.5 volume ratio) were dissolved in 50 mL of 1 M HCl and then transferred to the chamber of autoclave. 5 mmol of metal powders were quickly added into the mixture and the reactor was sealed subsequently. The reactor was heated to target temperatures without stirring and held for 5 min up to 12 h. Ramp rate is fixed at 5 °C/min for conventional heating and operating power of microwave is fixed at 90 W with 6s on and 24 s off cyclic mode for microwave heating. The temperature was monitored at the surface of glass vessel by portable IR thermometer in MW section. After finish each experiments, the reactor was left to cooldown to room temperature and the dispersion was filtrated to collect the as-prepared product. The post synthesis was carried out by the sonication of obtained powder with 5%v/v diluted $HNO_3$ solution for 10 min and then the suspension was filtrated and washed with distilled water and hot ethanol for a few times. The selected reaction conditions were summarized in Table 1. An additional experiment was also performed to investigate the effect of indium precursor. The individual $In(NO_3)_3$ was used instead of $InCl_3$ in experimental condition of 5 min MW heating and 6 h 105 °C conventional heating.

**Characterization**: The crystal phase of obtained products was determined by X-ray diffraction (XRD) (MiniFlex 600, Rigaku Denki, Japan) using CuK$\alpha$ radiation at a wavelength of 1.5406 Å with a scan step of 0.05° in $2\theta$ and a scan speed of 10°/min.

The morphology and size of the particles were examined using field emission scanning electron microscopy (FE-SEM) (JSM-6335F, JEOL, Japan) and transmission electron microscopy (TEM) (JEM-2010, JEOL, Japan). Before TEM analysis, the as-prepared particles were then suspended in ethanol and followed by sonication for 15 min prior to being dropped onto a TEM copper grid. The average diameters were determined by Scherrer's equation and randomly sampling more than 100 particles from SEM and TEM images.

**Table 1**. Experimental conditions of InAs synthesis

| Temperature (°C) | Time (h) | Heating source | Volume (%)† |
|---|---|---|---|
| 120 | 6 | Furnace | 75 |
| 120 | 6 | Furnace | 50 |
| 120 | 6 | Furnace | 25 |
| 105 | 6 | Furnace | 25 |
| 105 | 12 | Furnace | 25 |
| 80 | 12 | Furnace | 25 |
| ~105 | 30 min | MW | 25 |
| ~105 | 10 min | MW | 25 |
| ~105 | 5 min | MW | 25 |

†Percentage of solution in reaction chamber. The solution's concentration is equivalence.

## 2.2 Results and Discussions

In hydrothermal system, there have been known that the pressure inside the reactor chamber plays a crucial role in enforcing the formation mechanism.[4] To investigate this effect on the InAs synthesis, three different conditions of inner pressure were performed. As listed in Table 2.1, the 200 mL reactor was filled with 50, 100, and 150 mL of starting solution for 25, 50 and 75 volume% sample, respectively. The XRD patterns of precipitated products (Figure 2.1) indicate that the polycrystaline multiphase powders were obtained. The broad peak set at $2\theta$ = 25.4, 42.1, and 49.9° agrees well with the major reflections of bulk InAs (Black vertical line, JSPDS No. 15-0869) indicating the formation of zinc blende InAs nanoparticles in all three conditions. Apart from InAs, the diffraction patterns indicate the existence of major indium metal phase and minor $In(OH)_3$ in the least filled sample and major $As_2O_3$ phase in the most filled sample. The three kinds of impurity were observed with minor InOOH phase in a half filled sample. This result suggests that the indium impurity species were kinetically formed at the low pressure. When the pressure was increased by applying more volume of reacting solution, the arsenic oxide phase was thermodynamically initiated to rebuild. The indium impurity species were also promoted at this moderate pressure, and then they were vanished by the higher compression due to their thermodynamically unstable in acid solution.

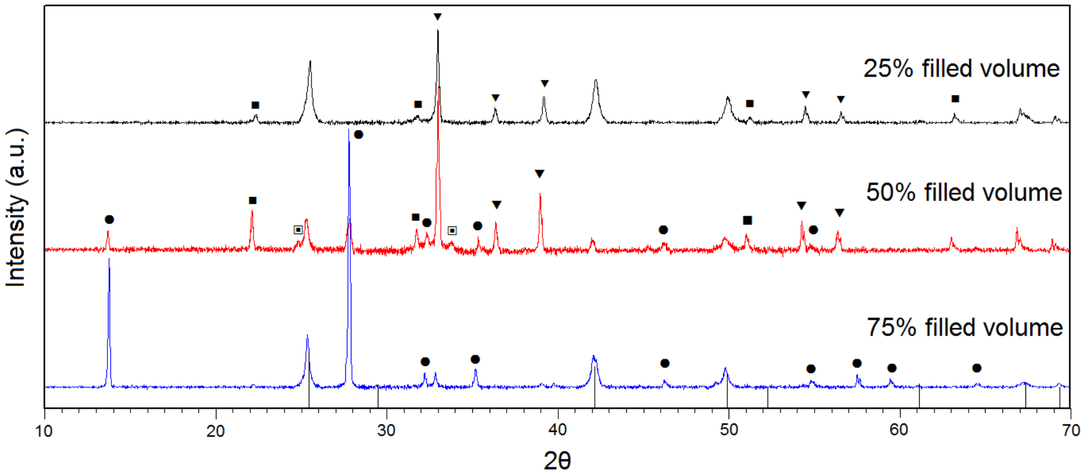

Figure 2.1 The diffraction patterns of obtained precipitates from three different filled volume in the reactor. The characteristic peaks of each compound were assigned by symbols; ▼: In, ■: $In(OH)_3$, ▣: InOOH, ●: $As_2O_3$.

In the reducing environment caused by excess zinc powder, arsenic ions were reduced to form arsine gas and some indium ions were slightly reduced to metallic indium. The arsine gas then reacted with free indium ions and produced InAs particle when the temperature was evaluated.[5] This step was promoted by the generated pressure inside reacting chamber through the increasing of kinetic energy as well as the interface affiliation. However, the supernumerary pressure can lead thermodynamically unstable arsine gas to be reoxidized with air and form more stable arsenic oxide phase.[6] The same phenomenon was occurred with indium ions when the system is aqueous solution.

The reaction behavior of hydrothermal system was further examined by lowering the reaction temperature and prolonging the reaction time. The operating temperature was dropped to 105 and 80 °C, and reaction time was extended to 12 h for both new temperatures. For an experiment at 105 °C, the sample with 6 h heat treated was also investigated. All samples were performed at 25% filled volume (50 mL in total).

Figure 2.2 shows the diffraction patterns of obtained precipitates from the reaction at 80 and 105 °C. The appearance of former impurity analogue was detected in all samples. At 80°C, the metallic zinc residue indicated that the reaction was not completed even the reaction time was extended to 12 h. Thus, the $As_2O_3$ might be obtained from the recrystallization of unreacted precursor in the starting solution when the reactor was cooling down, and there is not the product from the oxidation of arsine. This result suggests that the InAs monophase could be obtained by applying relatively long reaction time at low temperature. In addition, a trace amount of metallic indium also indicates the less reduction process of indium ions during the reaction. Hence, the formation of indium metal in this system is kinetically controlled, which means the avoiding of this reduction process requires high operated temperature and/or long reaction time. This viewpoint agrees well with the previous experiment. However, the high temperature synthesis and/or time consuming reaction are not the intention of this chapter.

The reaction at 105 °C for 6 h produced nearly the same product as obtained at 120 °C, and the prolonged experiment at 105 °C did not fabricate the significant benefit. $As_2O_3$ crystals was also formed along with the degrading of metallic indium and $In(OH)_3$

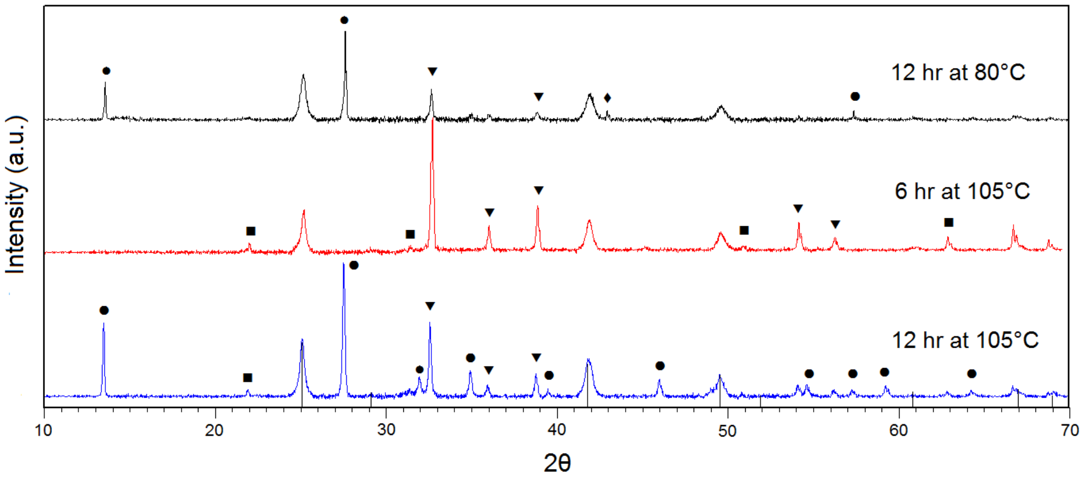

Figure 2.2 The diffraction patterns of obtained precipitates from the reaction at low temperature. The characteristic peaks of each compound were assigned by symbols; ▼: In, ■: $In(OH)_3$, ●: $As_2O_3$, ♦: Zn.

In the same way with the pressure effect, the arsenic oxide is the most thermodynamic stable compound in the experiment system.When the more energy was applied, by increasing the pressure, temperature, or time, the $As_2O_3$ are tended to recrystallize progressively along with the crystal growth of InAs, while the former kinetically stable metallic indium is converted to other species (especially InAs). On the other hand, trace $In(OH)_3$ is generally formed when the reaction temperature is higher than 100 °C and favored to growth at moderate pressure.

Since the crystalline InAs nanocrystals could be obtain at 80 °C. The further investigations employ MW energy to be an alternative heating source. The 25% filled volume of starting solution (45 mL in total) was used in every MW experiments. The experiment was carried out, at 25% filled volume with the same concentration of reactants as used in conventional heating, in three different reaction times, 5, 10, and 30 minutes, The maximum inner pressure was recorded during the reaction, which contribute to 2.1 MPa, 2.8 MPa, and 4 MPa in order of lengthening of reaction time. When the operating MW mode is cyclic, the temperature observed from IR sensor was fluctuated around 95 - 105 °C.

The XRD pattern of the MW samples with different exposure duration was shown in Figure 2.3. The characteristic diffraction of zinc blende InAs was observed in all reaction as a minor phase. This phenomenon could be interpreted in the effect of rapid heating from MW. Since the reaction is rapid, the two-phase reaction of indium ions in solution and arsine gas was not fully completed in short time whereas the reduction of indium is more favored due to the dramatically increasing of transformed MW energy.[7] The overall reaction did not complete at 5 minute duration because the evidence of zinc residue observed in the diffraction pattern. After 10 minute, all metallic zinc was oxidized and only InAs and $In^0$ phase were obtained, and The $As_2O_3$ was revealed in the prolonged reaction as expected. In addition, No hydroxide species of indium was observed. The low temperature (< 105 °C) and discontinuous heating of MW might be benefited in this manner.

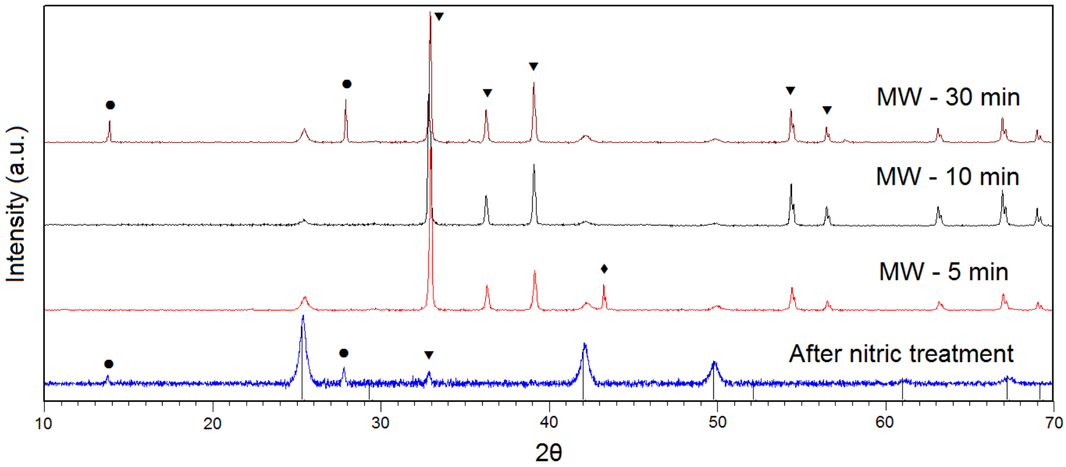

Figure 2.3 The diffraction patterns of obtained products from the MW reaction and the nitric acid treatment of MW-10 min sample. The characteristic peaks of each compound were assigned by symbols; ▼: In, ■: $In(OH)_3$, ●: $As_2O_3$, ♦: Zn.

The product of MW- 10 min sample was then treated with 5%v/v nitric acid to eliminate the indium metal.[8] The XRD pattern of treated sample was also rescaled for better visualization and shown in the Figure 2.3 (blue bottom line). However, a few residue of metallic indium was still observable as well as the arsenic oxide that formed during the acid treatment. Average crystallite sizes of InAs estimated by the Scherrer's equation[9] based on half-width of XRD peaks (θ = 0.315°) are about 26.5 nm. Size and morphology were further investigated by electron microscopy techniques. Figure 2.4 shows the SEM images of InAs nanoparticle with the aggregated polycrystalline form. There are likely spherical in shape with the average crystallite sizes of 52.5 nm. This value is larger than that obtained from the XRD patterns significantly because the wide range of appearance size observed in SEM and the coexistence of the amorphous phase. The TEM image of corresponding sample was shown in Figure 2.5. Irregular shape crystal and some amorphous can be seen in this image. The crystallite sizes were estimated at 30 nm that are in acceptable agreement with XRD result. However, the size of the particles of polycrystalite materials is hard to determine exactly.

The changing of indium precursor from $InCl_3$ to $In(NO_3)_3$ did not show any advantages in neither conventional heating nor microwave heating. In contrast, InAs was not obtained by using this precursor. The reason is the reduction potential to form arsine gas in the system was disturbed by the reactive nitrate ions, which tend to form nitrogen monoxide and nitrogen dioxide species. Another effect is suspected to be the higher concentration of oxygen in the system that promotes the production of Indium oxide species. The use of nitrate salts of indium in reduction system should be redesigned in further study.

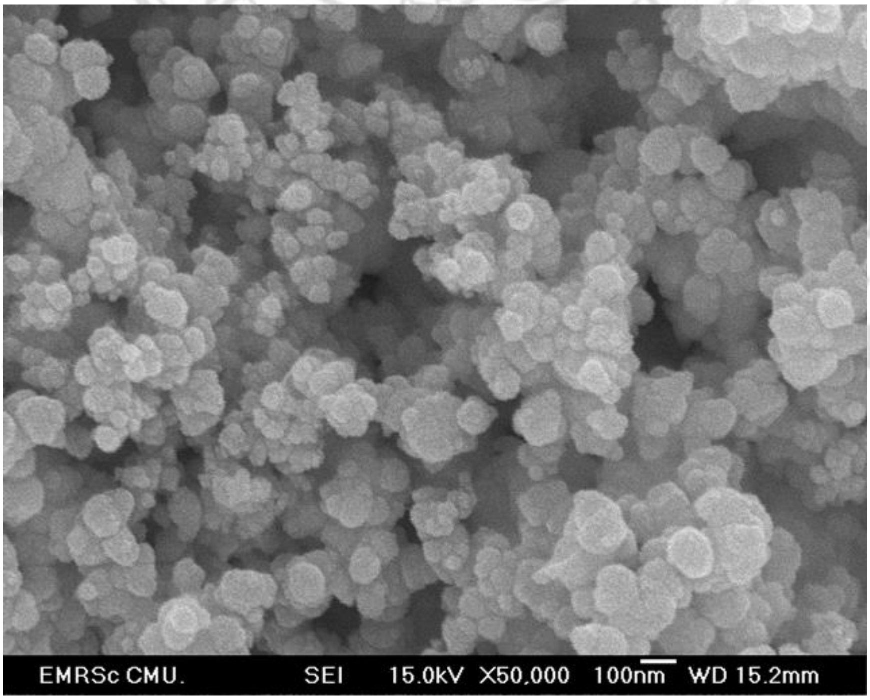

Figure 2.4 SEM image of InAs nanoparticles after nitric treatment

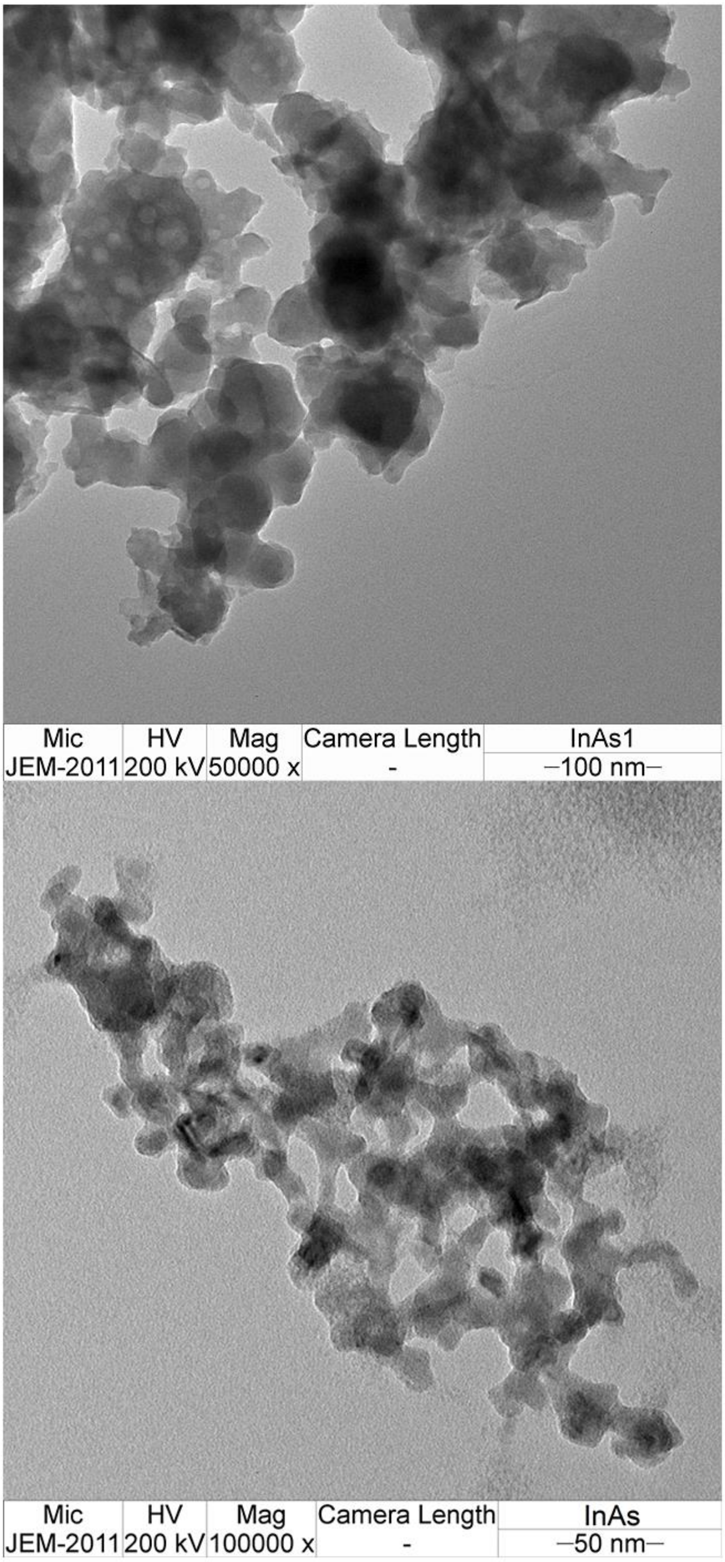

Figure 2.5 TEM image of InAs after nitric treatment

## 2.3 Conclusion

In summary, InAs nanoparticles were successfully synthesized via MW-assisted hydrothermal and conventional hydrothermal method. The product quality is acceptable with the assistance of post synthesis treatment. The reaction time was reduced to more than 30 folds faster when the MW is applied. Characterization indicates the zinc blende structure with the approximately size of 26.5 – 52.5 nm.

The effect of condition parameter in the hydrothermal system such as pressure and temperature was investigated. The formation behavior of products in this system was examined. The results indicate that the InAs nanoparticles were formed by the reaction of indium ions in the solution and arsine gas. While the impurities and impairments were occurred via 3 mechanisms: (i) The competitive reduction of indium ions to metallic indium by zinc powder. This process is kinetically controlled, which tend to be facilitated with rapid heating by MW energy. (ii) The neutralization of indium ions and/or the hydrolysis of indium to form $In(OH)_3$ and InOOH. This process is generally occurred in aqueous solution when the temperature is equal or more than 105 °C. The pressure around 4 MPa can promote this process, but the discontinuous heating e.g. MW heating acts in opposite way. (iii) Arsine gas can be reoxidized with oxygen in air to fabricate $As_2O_3$ crystal. This process is thermodynamically controlled, which tend to be facilitated by high pressure and/or long reaction time.

# References

[1] Vurgaftman, I., Meyer, J. R., & Ram-Mohan, L. R. (2001). Band parameters for III–V compound semiconductors and their alloys. *Journal of applied physics*, *89*(11), 5815-5875.

[2] Efros, A. L., & Rosen, M. (2000). The Electronic structure of semiconductor nanocrystals 1. *Annual Review of Materials Science*, *30*(1), 475-521.

[3] Lu, J., Wei, S., Yu, W., Zhang, H., & Qian, Y. (2004). Hydrothermal route to InAs semiconductor nanocrystals. *Inorganic chemistry*, *43*(15), 4543-4545.

[4] Yang, J., Zeng, J. H., Yu, S. H., Yang, L., Zhang, Y. H., & Qian, Y. T. (2000). Pressure-controlled fabrication of stibnite nanorods by the solvothermal decomposition of a simple single-source precursor. *Chemistry of materials*, *12*(10), 2924-2929.

[5] Zhang, J., & Zhang, D. (2010). Photoluminescence and Growth Kinetics of High-Quality Indium Arsenide and InAs-Based Core/Shell Colloidal Nanocrystals Synthesized Using Arsine (AsH3) Generated via Zinc Arsenide as the Arsenic Source. *Chemistry of Materials*, *22*(4), 1579-1584.

[6] Soignard, E., Amin, S. A., Mei, Q., Benmore, C. J., & Yarger, J. L. (2008). High-pressure behavior of As2O3: Amorphous-amorphous and crystalline-amorphous transitions. *Physical Review B*, *77*(14), 144113.

[7] Nadagouda, M. N., & Varma, R. S. (2007). Preparation of Novel Metallic and Bimetallic Cross-Linked Poly (vinyl alcohol) Nanocomposites under Microwave Irradiation. *Macromolecular rapid communications*, *28*(4), 465-472

[8] Hepler, L. G., Hugus Jr, Z. Z., & Latimer, W. M. (1953). The Stability of the Lower Oxidation States of Indium in Aqueous Solution. *Journal of the American Chemical Society*, *75*(22), 5652-5654.

[9] Monshi, A., Foroughi, M. R., & Monshi, M. R. (2012). Modified Scherrer equation to estimate more accurately nano-crystallite size using XRD. *World Journal of Nano Science and Engineering*, 2(03), 154-160.