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One-Pot Synthesis and Characterization of Chalcopyrite CuInS₂ Nanoparticles

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We synthesized tetragonal Chalcopyrite CuInS₂ (CIS) nanoparticles from molecular single source precursors, (Ph₃P)₂Cu-(μ-SEt)₂In(SEt)₂, by a one-pot reaction in the present of 3-mercaptopropionic acid at the reaction times of 3 hours or less with high-yields. In our approach, NaCl as by-product was used as heat transfer agent via conventional convective heating method. We tuned the sizes of nanoparticles through manipulation of reaction temperature, reaction time, precursor, and thiol concentration. The sizes of nanoparticles from 1.8 nm to 5.2 nm were obtained as reaction temperatures were increased from 150 °C to 190 °C. The method developed in this study is scalable to achieve ultra-large quantities production of tetragonal Chalcopyrite CIS nanoparticles. The resulting nanoparticles were analyzed by UV-Vis, X-ray diffraction, EDAX, and HRTEM.

Introduction

Quantum dot (QD) based solar cells have attracted much attention due to their potential to replace thin film devices.¹⁻³ One of the major advantages of employing QDs is simply changing the particle size to absorb specific wavelengths ranging from visible to infrared wavelengths.⁴ Incorporating varying sizes of nanoparticles in multiple layers, one may achieve increased solar energy absorption in photovoltaic devices.⁵⁻⁶ In order to facilitate QD based multilayer devices, synthetic strategies that can deliver QDs in *high yields* with precise size control are essential. Early examples used costly molecular beam epitaxy processes, but alternative inexpensive fabrication methods have recently been developed. One of the strategies to prepare QDs is to prepare nanoparticles from molecular single source precursors (SSPs).

Various I-III-VI₂ (i.e. CuIn_xGa_{1-x}S_ySe_{2-y}, where 0 ≤ x and y ≤ 1) semiconductor materials have been identified as promising photovoltaic materials, since devices containing CuIn_xGa_{1-x}Se₂ thin films, also known as CIGS, have already achieved superior efficiency.⁷⁻¹² Other applications are light-emitting devices and bioimaging techniques by tunable of luminescence properties of I-III-VI nanocrystals were discussed.¹³ For CuInS₂ QDs, the Wannier-Mott bulk exciton radius is approximately 8 nm with a bandgap of 1.45 eV and QDs with radii smaller than 8 nm exhibit bandgaps greater than 1.45 eV.⁴ There have been several reports on the formation of CuInS₂ nanoparticles through the decomposition of SSPs using thermolysis,¹⁴⁻¹⁹ photolysis,²⁰ and microwave irradiation.²¹⁻²⁴ Each SSP molecule contains the requisite elements to form CuInS₂ semiconductor materials, offering a unique level of control over product stoichiometry during the decomposition process. However, many of these procedures require combination of long reaction times of 10 to 24 hours (excluding the reaction time for preparation of SSPs) and high reaction temperatures often exceeding 200 °C. Pak *et al.*, recently developed an effective approach that affords (Ph₃P)₂Cu-(μ-SEt)₂In(SEt)₂ in 94% yield on a 500 g scale.²⁵ Pak *et al.*, also synthesized high yield Chalcopyrite CuInS₂ nanoparticles by decomposing SSPs via microwave irradiation in the presence of 1,2-ethanedithiol at reaction temperatures as low as 100 °C with reaction times as short as 30 min.²¹⁻²⁴ However, this procedure requires filtration or separation of by-product (NaCl),

evaporation of solvents, and re-dissolve of SSP for further reactions. The SSPs are not only exposed to air but also time consuming by these multi-steps.

The growth of nanomaterials is dependent on the thermodynamic and kinetic barriers in the reaction as defined by the reaction trajectory and influenced by vacancies, defects, and surface reconstruction events. For the most part, the synthetic methods utilize conventional convective heating due to the need for high-temperature initiated nucleation followed by controlled precursor addition to the reaction. Conventional thermal techniques rely on conduction of blackbody radiation to drive the reaction. The reaction vessel acts as an intermediary for energy transfer from the heating mantle to the solvent and finally to the reactant molecules. This can cause sharp thermal gradients throughout the bulk solution and inefficient, non-uniform reaction conditions. This is a common problem encountered in chemical scale-up and is made more problematic in nanomaterials where uniform nucleation and growth rates are critical to material quality.

Herein, we report the one-pot synthesis of Chalcopyrite CuInS_2 nanoparticles by decomposition of SSPs in the presence of 3-mercaptopropanoic acid via conventional convective heating method. The advantage of this reaction can be seen in the simplicity of the straightforward reaction and low-cost preparation of CIS nanoparticles. As we looked to overcome the slightly air sensitive SSPs and time consuming for separation of by-product (NaCl), evaporation of solvents, and re-dissolve of SSP for further reactions, we discovered that reacting of SSPs containing NaCl , as by-product, can provide desired products without sacrificing yield, processing time, and expose SSPs to air. We also discovered that NaCl acts as an intermediary for energy transfer from the heating mantle to the solvent and finally to the reactant molecules.

Experimental Section

Materials

Triphenylphosphine (Ph_3P , 99+%), indium (III) chloride (InCl_3 , anhydrous 99.999%, metals basis), copper (I) chloride (CuCl , anhydrous, 99.999%, metals basis), and benzyl acetate ($\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{CH}_3$, 99%) were purchased from Alfa Aesar. Ethanethiol

($\text{CH}_3\text{CH}_2\text{SH}$, 99+%) and 3-mercaptopropionic acid ($\text{HSCH}_2\text{CH}_2\text{CO}_2\text{H}$, 99+%) were purchased from Acros Organics. Ethyl ether ($(\text{CH}_3\text{CH}_2)_2\text{O}$, anhydrous, BHT stabilized/certified ACS) was purchased from Fisher Scientific. All other reagents were obtained from commercial sources and used without further purification. Unless stated otherwise, all reactions were performed in a fume hood, under inert conditions (dry nitrogen atmosphere) obtained by implementation of standard Schlenk techniques. Sodium ethanethiolate was prepared by refluxing ethanethiol (215.2 mL) over sodium metal (66.8 g, cut into small pieces, size $\sim 0.5\text{-}1\text{ cm}^3$) in a suspension of diethyl ether (800 mL) for overnight under N_2 . Precipitated sodium ethanethiolate was filtered and washed twice with fresh diethyl ether to remove any excess of ethanethiol. The product was then dried in *vacuo* to provide white powder and stored under nitrogen atmosphere.

Synthesis of Molecular Single Source Precursors (SSPs)

Single source precursor was synthesized according to improved procedures as shown in Fig. 1. Benzyl acetate was used as a solvent without further purification or drying. The synthesis of CIS SSPs includes three simple steps: 1) 2 molar equivalents (10.00 g, 38.13 mmol) of Ph_3P (triphenylphosphine) and 1 molar equivalent (1.885 g, 19.06 mmol) of anhydrous Cu(I)Cl (copper (I) chloride) were mixed with 100 mL of benzyl acetate in a round-bottom flask (either one or two neck) and stirred at 80 °C for 4 hrs under nitrogen atmosphere. (We first dissolved Ph_3P in benzyl acetate and then we added Cu(I)Cl .) White suspensions including the intermediate product $(\text{Ph}_3\text{P})_2\text{Cu-Cl}$ were formed in the first step. 2) 1 molar equivalent (4.22 g, 19.06 mmol) of anhydrous InCl_3 (indium (III) chloride) was added at 80 °C and kept stirring for another 1 hr under N_2 . The solution turned essentially clear with a light yellow color. We obtained the Cu-In coordination compound. 3) NaSEt (7.000 g, 83.21 mmol, 4.366 equiv) was added to this solution and stirred for an additional overnight at 80 °C. This series of steps ends with a crude suspension of the CIS SSPs in sodium chloride. At this point, there was no filtration or separation of sodium chloride as by-product and there was no evaporation of the solvent.

Synthesis of CuInS_2 (CIS) Nanocrystals

To the crude suspension of CSI SSPs prepared above, 3-mercaptopropionic acid (7.5 mL) was added as neat. The reaction mixture was heated achieving reaction temperatures from 150 °C to 190°C as desired for about 3 hours under N₂. Upon completion, the reaction was cooled to room temperature to yield precipitation of CuInS₂ nanoparticles. The resulting nanoparticles were isolated from the benzyl acetate solution by centrifugation, collected, and washed one time with CH₃OH, two times with 75:25 (v/v) mixtures of CH₃OH and H₂O, and two more time with CH₃OH. The product was then dried in *vacuo* to provide yellow to dark-orange powder. This method has been successfully adapted to prepare up to 5 g of nanoparticles in a single 250 mL reaction vessel.

Characterization

Transmission electron microscopy (TEM) images were taken with a JEOL JEM 2100 transmission electron microscope using a LaB₆-Cathode and an acceleration voltage of 200 kV. Energy-dispersive X-ray (EDX) analysis was also conducted on a JEOL JEM 2100 transmission electron microscope equipped with a Sapphire Si(Li) detecting unit from EDAX, using an acceleration voltage of 200 kV.

Powder X-ray diffraction (XRD) patterns were acquired with a PANalytical X'Pert Pro X-ray powder diffraction system using incident beam hardware: Ceramic tube (Cu anode), soller slit 0.04 radians, divergence slit 1/2, mask 10 mm and diffracted beam hardware: anti-scattering slit 1/2, Ni-filter, receiving slit 1/4, soller slit 0.04 radians, proportional detector (Xe-filled). Scans were collected for 25 min employing a 0.06° step width at a rate of 2 s/step resulting in a 2θ scan range from 20-65°.

Absorption spectra of nanoparticles were obtained from the UV-Vis data recorded on a Perkin Elmer Lambda 950 spectrophotometer. A plane glass was measured as the background transmission at room temperature.

Results and Discussion

We improved our previous procedures (as described in Ref. 25) to synthesize the single source precursors. In our experiments, high boiling point solvent (i.e. benzyl acetate) was

applied without further purification or drying. For SSP synthesis, there are three simple steps reactions as shown in Fig. 1. 1) Ph_3P (2 equiv), benzyl acetate and CuCl (1 equiv) were heated for 4 hrs at $80\text{ }^\circ\text{C}$ to form a white suspension including the intermediate product $(\text{Ph}_3\text{P})_2\text{Cu-Cl}$. (We first dissolved Ph_3P in benzyl acetate and then we added Cu(I)Cl .) 2) Anhydrous InCl_3 (1 equiv) was added and stirred for about 60 min at $80\text{ }^\circ\text{C}$ to form the Cu-In coordination compound. 3) NaSEt (4.366 equiv) was added and stirred for an additional overnight at $80\text{ }^\circ\text{C}$ to obtain CIS SSPs. Similar mechanism of chemical reactions was discussed in our previous work.²⁵ The result starting materials, single source precursor (SSPs), are slightly air-sensitive and are stored in an argon filled inert atmosphere drybox (Vac Atmospheres) to prevent decomposition. Accordingly, we eliminated steps involving filtering, evaporating, and drying of SSP. This enables the formation of SSP complexes without expose to the air. We have efficiently synthesized CuInS_2 (CIS) nanocrystals by one-pot reaction, first mixing and forming a clear solution mixture of the SSP at $80\text{ }^\circ\text{C}$ and then heating up the mixture to a temperature of $150\text{-}190\text{ }^\circ\text{C}$ in 3-mercaptopropanic acid for product formation (CIS nanocrystals) via conventional heating technique.

We have determined that the optimal temperature for formation of CIS nanocrystals is around $150\text{ }^\circ\text{C}$, which is lower than the widely reported reaction temperatures via conventional heating technique. Hepp *et al.*¹⁴ synthesized CIS nanocrystals at temperatures above $200\text{ }^\circ\text{C}$. At $200\text{ }^\circ\text{C}$, the CIS was not formed, only intermediate precursor comprising a mixture of Cu_xS_y and In_xS_y as hypothesized. These results suggest that in order to avoid formation of the intermediate precursor the optimal temperature for the synthesis of CIS nanocrystals should be above $200\text{ }^\circ\text{C}$. Our strategy for avoiding the formation of the intermediate precursor was to first form the SSP complexes without filtration or separation of sodium chloride. We hypothesized that the sodium chloride could be the heat agent, which could transfer heat from the reaction flask to SSP more effectively.

Hepp *et al.* observed formation of CIS nanoparticles in 5 hours using traditional heating methods. The total reaction time and work up for synthesis of CIS nanocrystals using our

procedure is much shorter than that reported for converting the SSP to CuInS₂ nanocrystals.¹⁴⁻²⁴ Sodium chloride is soluble in both water (359g/L) and methanol (14.9 g/L)²⁶ and the solubility of sodium chloride in water, methanol, ethanol, and their mixed solvents had been studied by Pinho and Macedo.²⁷ First nanoparticles were isolated from the benzyl acetate solution by using 100% methanol to remove most of the solvent and other impurities. Then mixture of CH₃OH and H₂O (75:25 by volume) was used to remove most of the sodium chloride. To ensure all of sodium chloride had been removed, the mixture of CH₃OH and H₂O (75:25 by volume) had been used to wash nanoparticles. Finally, nanoparticles were washed two more time with 100% methanol.

Figure 1 displays a standard route in forming CuInS₂ nanoparticles. The process includes adding 2 molar equivalents of Ph₃P (triphenylphosphine) to 100 mL of benzyl acetate to form a solution; adding 1 molar equivalents of anhydrous CuCl and anhydrous InCl₃ to the stirring solution; adding 4 molar equivalents of precursor forming material NaSEt; and adding 3-mercaptopropionic acid to form a reaction mixture. The reaction mixture was then exposed to heat and maintained at temperatures in a range of from 150° C to 190° C for about 2 hours to form CuInS₂ particles in the chalcopyrite phase (i.e., CuInS₂ chalcopyrite particles). As previously indicated, reaction temperature, reaction time and concentration of single source precursors and a thiol concentration were controlled to form various sizes of the CuInS₂ chalcopyrite particles. The insert shows the resulting color change of the nanoparticles that settled at the bottom of sample vessels. Progressively darker colors represent higher reaction temperatures representing respective sizes of CuInS₂ nanoparticles from small to large.

Figure 2 shows the electron diffraction and HRTEM structure images of CuInS₂ nanoparticles prepared from SSPs in presence of 3-mercaptopropionic acid in benzyl acetate at 170 °C. By our best observation, the nanoparticles appear to have about 4 nm diameters with narrow size distribution. According to the EDAX data, all particles formed in our studies consist of Cu, In, and S. The nanoparticle sizes from 1.8 nm to 5.2 nm were confirmed by evaluation of HRTEM images as reaction temperatures were varied from 150 °C to 190 °C. The nanoparticle sizes from yellow to dark-orange were

confirmed by evaluation of the XRD data (Figure 3). We determined volume-weighted crystal diameters (Scherrer equation with a shape factor of 0.9).²⁸ In particular, the XRD patterns show the CuInS₂ nanoparticles are crystalline with the Chalcopyrite phase with major peaks at $2\theta = 28, 46,$ and 55° attribute to (112), (204) and (116) phases. The peaks are consistent with tetragonal CuInS₂ reference pattern 85-1575 (JCPDS-03-065-2732). This is consistent with our electron diffraction analysis. Furthermore, a careful evaluation of the gradual sharpening of the peaks in the XRD spectra is indicative of the increasing particle sizes with increasing reaction temperatures. The absorption behaviors of the nanoparticles showed the expected blue-shift with decreasing sizes which represent small to large bandgaps (Figure 4).

We also further observed that size control based on concentration of 3-mercaptopropionic acid. For example, in the absence of thiol, Chalcopyrite nanoparticles were not produced at below 200 °C.¹⁵ It was determined that at least 7.5 mL of 3-mercaptopropionic acid was required to produce Chalcopyrite nanoparticles. When 25mL of 3-mercaptopropionic acid was used as the reaction solvent at 170 °C, the largest Chalcopyrite nanoparticles were collected. The absorption behaviors of the nanoparticles showed the expected blue-shift with decreasing sizes as decreasing concentration of 3-mercaptopropionic acid which represent small to large band gaps as shown in Figure 5.

Conclusion

Potentially, these nanocrystals can be incorporated into next-generation quantum-dot-based solar cells. We have shown that by exploiting the conventional convective heating method one-pot decomposition of single source precursors to afford CuInS₂ nanoparticles in the presence of 3-mercaptopropionic acid and NaCl as by product. We can prepare CuInS₂ nanoparticles with diameters ranging from 1.8 - 5.2 nm with very high-yield of Chalcopyrite CuInS₂ nanoparticles. Short reaction times of 3 hours or less are required for the preparation of these nanoparticles. The reaction temperature and 3-mercaptopropionic acid concentration are all critical for fine control of nanoparticle size. Gram quantities of CuInS₂ nanoparticles can be obtained by the method developed in this

study, demonstrating its potential for providing ultra-large quantities of tunable I-III-VI₂ compound nanoparticles with small amount of solvent in applications for low-cost non-vacuum-based CIS solar cells.

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Notes

The authors declare no competing financial interest.

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Figure Captions:

Figure 1: A general illustration for steps forming CuInS₂ nanoparticles. The insert shows CuInS₂ nanoparticles prepared from SSPs in presence of 3-mercaptopropionic acid in benzyl acetate at 150, 170, and 190 °C respectively from left to right.

Figure 2: Electron diffraction and HRTEM structure analysis of CuInS₂ nanoparticles prepared from SSPs in presence of 3-mercaptopropionic acid in benzyl acetate at 170 °C.

Figure 3. XRD data of CuInS₂ nanoparticles prepared at 170 °C.

Figure 4. UV-Vis absorption spectra of typical CuInS₂ nanoparticles prepared from 150 to 190 °C respectively.

Figure 5. UV-Vis absorption spectra of typical CuInS₂ nanoparticles prepared from 7.5, 15, and 25 mL 3-mercaptopropionic acid respectively from left to right in benzyl acetate at 170 °C.

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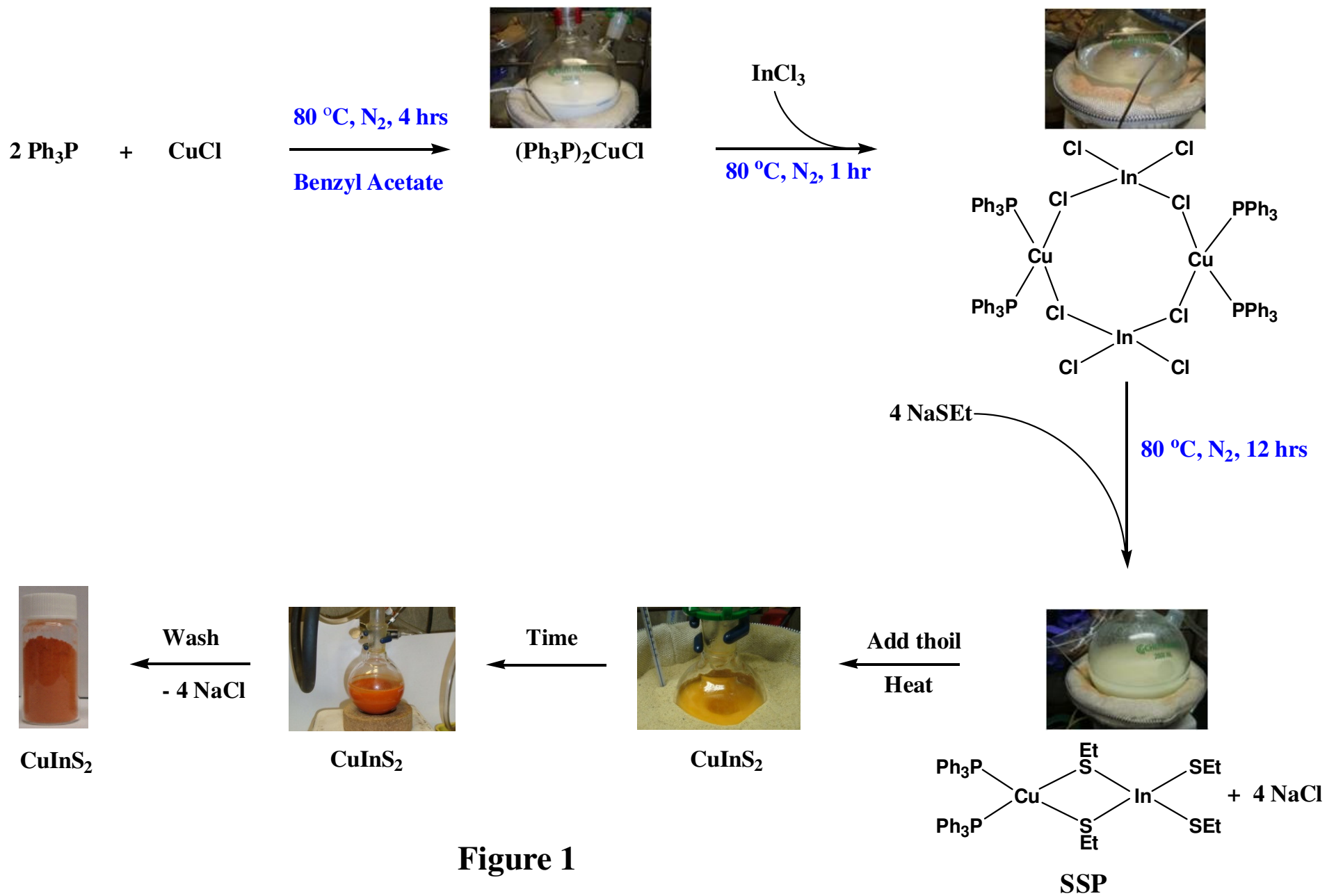
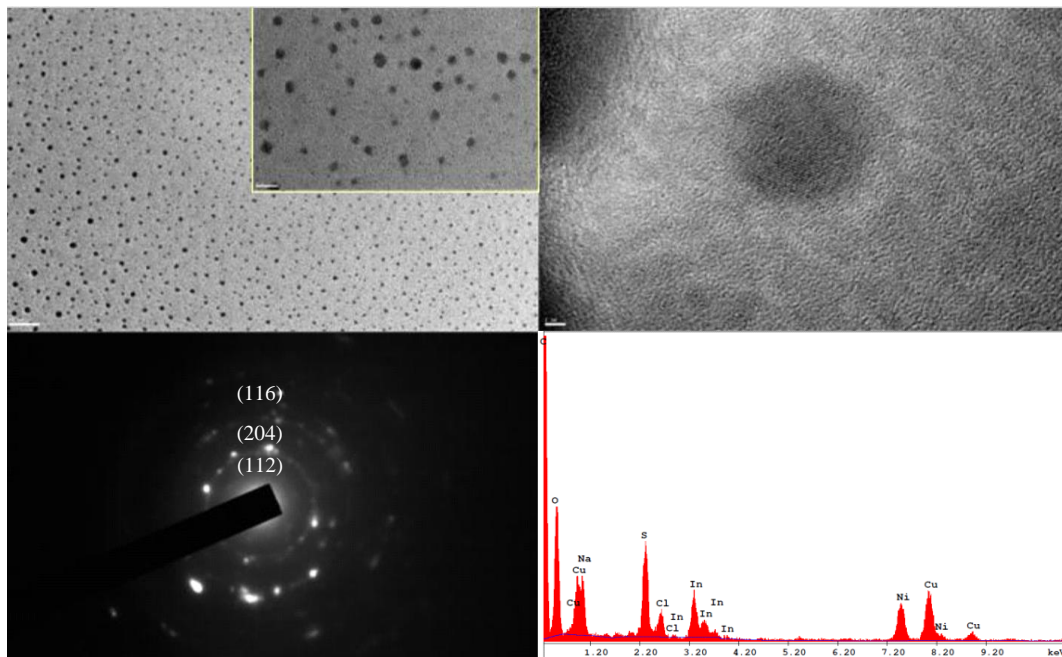


Figure 1

**Figure 2**

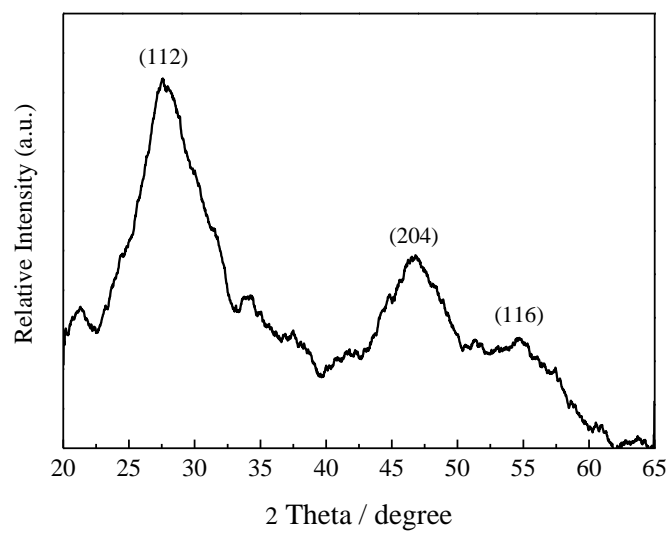


Figure 3

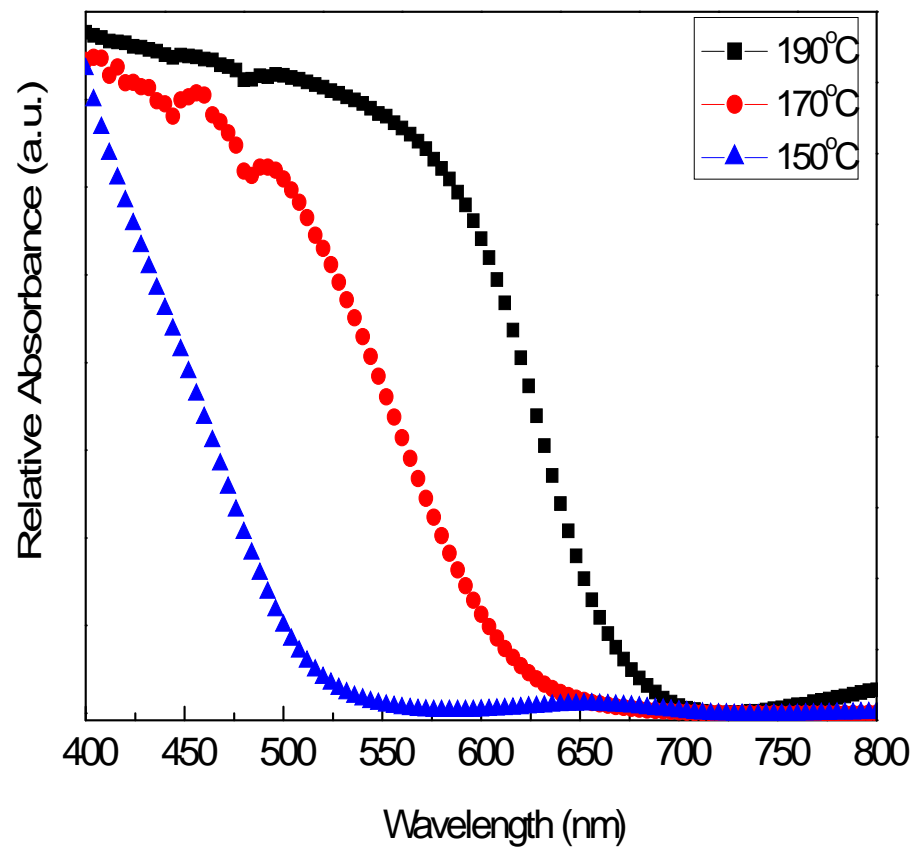


Figure 4

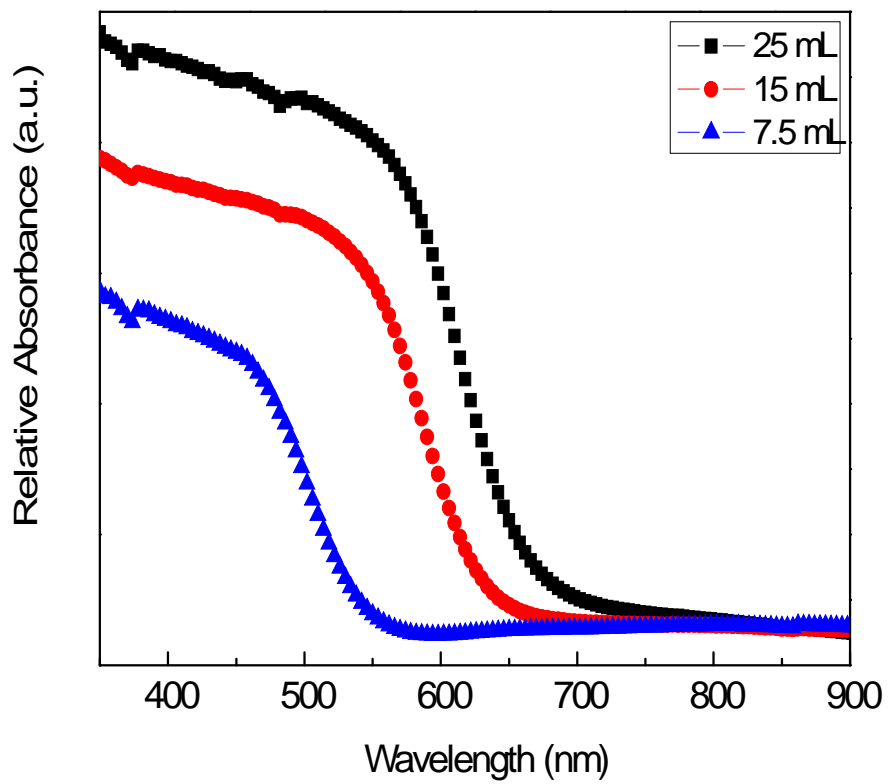


Figure 5