The phase transformation of CuInS$_2$ from chalcopyrite to wurtzite

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Abstract

In the present work, CuInS$_2$ nanoparticles have been successfully synthesized by water-bath method with deionized water as solvent and thioglycolic acid as complexing agent at 80°C. The phase transition of CuInS$_2$ from chalcopyrite to wurtzite was realized by adjusting the pH value of reaction solution. The emergence of Cu$_2$S in the condition of higher pH value of reaction solution led to the formation of wurtzite CuInS$_2$. This facile method that controls the phase structure by adjusting the solution pH value could open a new way to synthesize other I-III-VI$_2$ ternary semiconductor compounds.

Keywords: Chalcopyrite; Wurtzite; pH; CuInS$_2$

Background

With increasing global energy consumption, the fabrication of pollution-free, low-cost, and high-efficiency photovoltaic cells has attracted successive attention in recent years. As an I-III-VI$_2$ ternary semiconductor compound with a direct bandgap of 1.5 eV at room temperature, CuInS$_2$ is a promising material for photovoltaic applications because of its low toxicity, high absorption coefficient, and high theoretical photovoltaic conversion efficiency (about 25% to 30%) [1-3].

In the previous studies, CuInS$_2$ has been found to exist in three different crystal structures: chalcopyrite, zinc blende, and wurtzite [4-6]. Chalcopyrite CuInS$_2$ is the most common existing phase at room temperature, whereas those with zinc blende and wurtzite structures are stable only at high temperatures. Different from those of chalcopyrite phase CuInS$_2$, the indium and copper atoms of wurtzite CuInS$_2$ are randomly distributed over the cation sites of the lattice which allows the flexibility of stoichiometry and easily tuning the Fermi energy over a wider range [1,7,8]. Due to the differences in structure, wurtzite CuInS$_2$ not only exhibits different optical properties but also may present novel properties which can expand its application. Therefore, it is meaningful to develop an effective route to realize the controlled synthesis of CuInS$_2$ with different phase structures. Most of the reports about controlling the phase structure of CuInS$_2$ were achieved by changing the ligand species or reaction temperatures. For example, Pan et al. firstly reported the synthesis of zinc blende- and wurtzite-structured CuInS$_2$ nanocrystals by changing the ligand species [9], and Sudip K et al. reported the synthesis of zinc blende- and wurtzite-structured CuInS$_2$ nanocrystals by changing the reaction temperature [10]. We also noted that for solution-phase reactions, the pH value of reaction solution can affect the complexation capability of complexing agent to metal ions, and it might be used to control the phase structure of products. Chai et al. has reported the synthesis of cubic and hexagonal phase ZnIn$_2$S$_4$ by adjusting the pH value of the reaction solution [11]. This method presents a simple and eco-friendly way for the controlled synthesis of ternary nanomaterials with tailored structures.

On the other hand, CuInS$_2$ in nanophase is usually synthesized in harsh conditions of high temperature and high pressure using organic solvent, which inevitably makes the reaction more difficulty controlled. In this report, we demonstrate the successful synthesis of chalcopyrite phase and wurtzite phase CuInS$_2$ by a simple water-bath method at relatively low temperature of 80°C under atmospheric environment. By using deionized water as the solvent and thioglycolic acid as the complexing agent, the phase transformation of CuInS$_2$ from chalcopyrite phase to wurtzite phase can be achieved by...
simply adjusting the pH value of the reaction solution as well as the annealing temperature. It has been found that CuInS$_2$ gradually transformed from chalcopyrite to wurtzite with the increase of pH value, and the wurtzite CuInS$_2$ gradually transformed to chalcopyrite phase with the increase of annealing temperature. To the best of our knowledge, this is the first report that controls the phase transformation of CuInS$_2$ from chalcopyrite to wurtzite by adjusting the pH value of the reaction solution. This work may provide a feasible reference for the simple and easy synthesis of different phase-structured I-III-VI$_2$ ternary semiconductor compounds.

**Methods**

**Materials**

All chemicals were used as received without further purification. Copper (II) chloride dihydrate (CuCl$_2$·2H$_2$O ≥ 99.0%), indium (III) sulfate anhydrous (In$_2$(SO$_4$)$_3$ ≥ 99.99%), sodium sulfide nonahydrate (Na$_2$S·9H$_2$O), and sodium hydroxide (2 mol/L NaOH solution) were all purchased from Tianjin Kernel Chemical Reagent Co. Ltd. (Tianjin, China). Thioglycolic acid (TGA) was obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The water used in all experiments was obtained from a Millipore Milli-Q purification system and had a resistivity higher than 18.2 MΩ·cm. All experiments were carried out in water-bath pot under atmosphere.

**Synthesis of CuInS$_2$ nanoparticles**

CuInS$_2$ was synthesized in aqueous solution via a water-bath approach. In a typical synthesis, 1 mmol CuCl$_2$ and 0.5 mmol In$_2$(SO$_4$)$_3$ were mixed with 20 mL of deionized water, then TGA aqueous solution as reducing and complexing agent (20 mmol TGA in 10 mL of deionized water) was added into the solution under constant stirring. The mixture became milky white quickly. Then, the pH value of the mixed solution was adjusted from 1.27 to 10.3 by adding aqueous NaOH solution (2 mol/L) to check the effects of pH value on the final product. Na$_2$S aqueous solution as sulfur source (2 mmol Na$_2$S was dissolved in 10 mL of deionized water) was then added to the mixture. After stirring for 30 min, the reaction mixture was heated to 80°C for 48 h under atmosphere conditions. Finally, the obtained solution was cooled down to room temperature. The precipitate was separated by centrifugation and washed several times with deionized water and anhydrous ethanol then dried at 60°C for 8 h.

**Characterization**

The phase and crystallographic structure of the prepared products were characterized by X-ray diffraction on a Bruker D8 Advance X-ray powder diffractometer (XRD) with Cu Ka radiation source ($\lambda = 0.15418$ nm). Scanning electron microscopy (SEM) images were acquired using a FEI Nova NanoSEM 450 scanning electron microscope (FEI, Hillsboro, OR, USA). Transmission electron microscopy (TEM) images were performed on a JEOL JEM-2010 electron microscope (JEOL, Akishima-shi, Tokyo, Japan) operating at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed with a Kratos Axis Ultra system using monochromatic Al Kα X-rays (1,486.6 eV). The UV-vis absorption spectra were obtained by using UV-vis Spectrometer (Perkin-Elmer, Lambda 950, Waltham, MA, USA). The simulated crystal structures and wurtzite XRD patterns of CuInS$_2$ were obtained by using Diamond 3.2 programs.

**Results and discussion**

By adjusting the pH value of the reaction solution, CuInS$_2$ nanoparticles with various phase structures have been successfully synthesized at the temperature of 80°C. Figure 1a shows the XRD pattern of the products synthesized with pH value of 1.27. All the diffraction peaks could be well indexed to (112), (204), and (312) planes of the standard chalcopyrite structure of CuInS$_2$ (JCPDS card file no. 85-1575), respectively. The diffraction peaks of the product are wide and weak, which indicates that the as-synthesized CuInS$_2$ nanoparticles have very small sizes or poor crystallinity [12]. Figure 1b shows the XRD pattern of the products synthesized at pH of 10.3. The peak position and relative peak intensities can match well with the powder diffrac tion data reported for wurtzite CuInS$_2$ [9,13-15]. The diffraction patterns were simulated using the lattice parameters previously reported for wurtzite CuInS$_2$ (simulated by using the software Diamond 3.2, with the space group of P63mc and lattice parameters $a = b = 3.897$ Å, $c = 6.441$ Å [9]), and it matched well with our experimental XRD diffraction pattern. The diffraction peaks located at 2 theta of 26.3°, 27.69°, 29.75°, 38.52°, 46.4°, 50.32°, 54.94°, 56.3°, and 70.96° can be assigned to the (100), (002), (101), (102), (110), (103), (112), (201), and (203) planes, respectively. No diffraction peaks from other species can be detected, which indicates that the obtained samples are pure wurtzite CuInS$_2$ without any binary sulfides of Cu$_2$S, CuS, or In$_2$S$_3$.

The morphology of the as-synthesized CuInS$_2$ was investigated by SEM, as shown in Figure 2. Figure 2a,d shows the SEM images of the as-synthesized chalcopyrite and wurtzite CuInS$_2$, respectively. It reveals that the product is composed of a large quantity of nanoparticles, which are easily agglomerated due to the high active surface of nanoparticles. Further investigation was carried out by TEM. Figure 2b shows that the as-synthesized chalcopyrite CuInS$_2$ has very small sizes which match well with the obtained wide and weak XRD patterns. Figure 2e shows that the as-synthesized wurtzite CuInS$_2$
has an irregular feature of shape. Figure 2c,f shows the selected-area electron diffraction (SAED) of chalcopyrite and wurtzite CuInS$_2$. In Figure 2c, three diffraction rings can be clearly seen, which can be well indexed as (112), (204), and (312) planes of the chalcopyrite CuInS$_2$, respectively. Figure 2f shows the polycrystalline feature of the as-synthesized wurtzite CuInS$_2$, according to the calculated lattice parameters based on the XRD pattern of wurtzite CuInS$_2$. The diffraction rings can be well indexed to (100), (101), (102), (103), (110), and (200) planes of wurtzite phase CuInS$_2$, respectively.

The influence of synthesis conditions on the crystal phase of products was studied by altering the pH value of reaction solution. Figure 3 shows the evolution of XRD patterns of the as-synthesized CuInS$_2$ nanoparticles prepared with increasing pH values of reaction solution. It was found that the pH value of reaction solution played an important role in the determination of phase structure of the final product. As shown in Figure 3, when the pH value of the solution was 1.27, the chalcopyrite CuInS$_2$ could be obtained. When the pH value of the solution increased to 5.3, the chalcopyrite CuInS$_2$ transformed into wurtzite CuInS$_2$. When the pH value of reaction solution is 10.3, the crystallization of the product is the best. Because of the Na$_2$S shows very strong alkaline, the final reaction solution changed to alkaline solution when sufficient Na$_2$S aqueous solution was added to the reaction solution with a pH value of 5.3.

According to Pearson’s Hard-Soft Acid-Base (HSAB) theory [16], a soft acid and a soft base bind more tightly than a soft base and a hard acid. Cu$^{+}$ is a soft acid, In$^{3+}$ is a hard acid, and the TGA is a soft base which will react preferentially with soft acid Cu$^{+}$ [17]. The Cu-SR bond should be stronger than the In-SR bond [12,18]. Therefore, the excess of TGA can balance the reaction rate between Cu$^{+}$ and In$^{3+}$ and S$^{2-}$.

Figure 1 XRD patterns of as-synthesized chalcopyrite and wurtzite CuInS$_2$. (a) Chalcopyrite. (b) Wurtzite. Insets show the corresponding crystal structures.

Figure 2 The morphology of the chalcopyrite and wurtzite CuInS$_2$. (a, d) SEM image, (b, e) TEM image, (c, f) SAED pattern.
From the phenomenon of the reaction process (Additional file 1: Figure S1), When the TGA is added into the mixture solution of Cu and In ions, the color of the solution changes from blue to creamy white, which indicates that CuIn(SR)\textsubscript{x} complex is generated in the solution. If the Na\textsubscript{2}S was directly added into the solution without adjusting the pH value of the solution (pH = 1.27), the color of the solution will change from creamy white to orange. However, if the pH value of the solution was adjusted to alkalinity (pH = 10.3), the creamy white solution will become a colorless transparent solution. When we add the Na\textsubscript{2}S into the solution, the color of solution becomes gray black.

From the phenomenon of the reaction process (Additional file 1: Figure S1), It can be found that the pH value of reaction solution indeed plays an important role in the reaction. The essence is that the pH value of solution influences on the complexation of TGA. The Cu\textsuperscript{2+} can be quickly reduced to Cu\textsuperscript{+}, and the CuIn(SR)\textsubscript{x} complex (creamy white) is formed when the TGA is added into the mixed solution of Cu\textsuperscript{2+} and In\textsuperscript{3+}, which makes the solution change from blue to creamy white because the Cu\textsuperscript{2+} is blue but Cu\textsuperscript{+} is colorless. As the pH value increases with the addition of NaOH, the CuIn(SR)\textsubscript{x} complex dissociates and releases Cu\textsuperscript{+} into solution, and the solution changes from a creamy white to a colorless transparent solution. When we add the Na\textsubscript{2}S into the solution, the color of solution becomes gray black.

According to the previous report, metastable wurtzite CuInS\textsubscript{2} may transform into chalcopyrite phase when wurtzite CuInS\textsubscript{2} is heated to a certain temperature [6,22]. Figure 4 shows the XRD patterns of samples obtained by annealing the wurtzite phase CuInS\textsubscript{2} at temperatures of 200°C, 300°C, 400°C, and 500°C, respectively. It shows that the characteristic peaks at 28° of chalcopyrite become more and more obvious with the increase of annealing temperatures. When the metastable wurtzite CuInS\textsubscript{2} was annealed from 200°C to 400°C, a coexistence stage of chalcopyrite phase and wurtzite phase CuInS\textsubscript{2} might exist. When the temperature reached 500°C, the wurtzite phase CuInS\textsubscript{2} completely transformed into chalcopyrite phase.

The chemical composition and valence states of wurtzite CuInS\textsubscript{2} were investigated by XPS analysis. The typical survey and high-resolution spectra in regions of Cu 2p, In 3d, and S 2p are shown in Figure 5. The survey spectrum in Figure 5a indicates that the product wurtzite CuInS\textsubscript{2} have a hexagonal structure; such a structural similarity induces the formation of wurtzite CuInS\textsubscript{2} [1,19].
contains Cu, In, and S elements. As shown in Figure 5b, the binding energies of Cu 2p\textsubscript{3/2} and 2p\textsubscript{1/2} were located at 931.9 and 951.7 eV with a peak splitting of 19.8 eV, respectively, which are in good consistence with the reported values for Cu\textsuperscript{+} [10,23]. In addition, the Cu 2p\textsubscript{3/2} satellite peak of Cu\textsuperscript{2+}, which is usually located at 942 eV, does not appear in the spectra [24]. Therefore, it can be concluded that the starting Cu\textsuperscript{2+} ions have been reduced to Cu\textsuperscript{+} by TGA. The In 3d\textsubscript{5/2} and 3d\textsubscript{3/2} peaks (Figure 5c) were located at 444.7 and 452.3 eV with a peak splitting

Figure 5 The XPS spectra of wurtzite CuInS\textsubscript{2}. (a) Survey spectrum, (b) Cu 2p, (c) In 3d, (d) S 2p.

Figure 6 The UV-vis absorption spectrum of chalcopyrite and wurtzite CuInS\textsubscript{2}. The insets show the bandgaps of the CuInS\textsubscript{2}.
of 7.6 eV, which matched well with that of In$^{3+}$. The S 2p has doublet peaks of S 2p$_{1/2}$ and 2p$_{3/2}$ due to the spin-orbit coupling [25]. The two peaks of S 2p (Figure 5d) were located at 161.7 and 162.8 eV, respectively, with a peak splitting of 1.1 eV, which can be assigned to S$^{2-}$. No obvious impurities could be detected in the sample.

Figure 6 shows the UV-vis absorption spectrum of the as-prepared chalcopyrite and wurtzite CuInS$_2$ measured at room temperature. Both the two phases of CuInS$_2$ show a broad and strong absorption in the visible region. Compared with chalcopyrite CuInS$_2$, the wurtzite CuInS$_2$ showed a higher and broader absorption in the entire visible region and near-infrared region. The bandgap can be determined by plotting ($a$h$v$)$^2$ versus $hv$ ($a$ = absorbance, $h$ = Planck’s constant, and $v$ = frequency) [26,27]. As shown in the inset picture, the calculated optical bandgap for chalcopyrite and wurtzite CuInS$_2$ is about 1.54 and 1.47 eV, respectively, which is close to the bulk energy bandgap of CuInS$_2$.

Conclusions
In summary, CuInS$_2$ in chalcopyrite and wurtzite phases has been successfully synthesized via a low-cost, facile water-bath method. The phase structure of as-synthesized CuInS$_2$ can be easily controlled by adjusting the pH value of the reaction solution. Low-cost thioglycolic acid plays a key role in the synthesis process of CuInS$_2$. Thioglycolic acid acts not only as a stabilizer and complexing agent to balance the reaction rate among Cu$^2+$, In$^{3+}$, and S$^2-$ but also as a reducing agent which can reduce Cu$^{2+}$ to Cu$.^+$. Compared with the traditional organic phase synthesis route, this method provides a feasible way that is much simpler, greener, and cheaper, in addition to the easy control of phase structure for the mass production of CuInS$_2$.

Additional file

Additional file 1: Figure S1. The phenomenon of the reaction process. Figure S2. XRD pattern of the as-grown products of gray black solution. Figure S3. XRD pattern of the products synthesized without thioglycolic acid.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
BBX and BBH carried out the experiments and wrote the manuscript. LFJ and GL participated in the experiment design and characterization of the sample. ZLD was the investigator who guided the whole experiments and the draft of the manuscript. All authors read and approved the final manuscript.

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