



## Phase control and its mechanism of CuInS<sub>2</sub> nanoparticles

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### ABSTRACT

CuInS<sub>2</sub> nanoparticles (NPs) usually take chalcopyrite-(CP) structure. Recently, CuInS<sub>2</sub> NPs with pseudowurtzite (WZ) structure, which is thermodynamically less favored, have been synthesized. However, the formation mechanism of this metastable-phase has not been understood yet. In this report, the key issue of phase selectivity of CuInS<sub>2</sub> (CIS) NPs has been investigated using various metal sources and ligands. Experimental results suggested that the crystalline structure and morphology of CIS NPs were decided by the stability of indium ligand complex; the active ligand reduces the precipitation rate of In<sub>2</sub>S<sub>3</sub>, resulting in pre-generation of Cu<sub>2</sub>S seed NPs. Crystallographic analogy and superionic conductivity of Cu<sub>2</sub>S remind us that the formation of WZ CIS NPs is attributed to the pre-generation of Cu<sub>2</sub>S seed NPs and the following cation exchange reaction. In order to confirm this hypothesis, Cu<sub>2-x</sub>S seed NPs with various structures have been annealed in indium–ligand solution. This experiment revealed that the crystalline structure of CIS NP was determined by that of pre-generation Cu<sub>2-x</sub>S NPs. Our results provide the important information for the phase control and synthesis of ternary chalcogenide NPs with a novel crystalline structure.

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## 1. Introduction

Solution-based synthesis processes have been developed to successfully synthesize various I–III–VI<sub>2</sub> chalcopyrite nanoparticles (NPs) [1–9]. Kino et al. succeeded to synthesize super fine CuInS<sub>2</sub> (CIS) NPs from the thermolysis of Cu–In thiolate in a hot ligand solvent [1]. Nose et al. and Koo et al. demonstrated the synthesis of CIS NPs by using the metathesis reaction between metal halides and sulfur powder in hot surfactant solutions [2,3].

Batabyal et al. introduced the single source precursor “(Ph<sub>3</sub>P)CuIn(SC(O)Ph)<sub>4</sub>” into CIS NP synthesis [4].

CIS NPs take two crystalline structures; stable “chalcopyrite” and metastable phase “pseudo-wurtzite” (WZ). It has been reported that an active ligand species plays an important role in the formation of CIS NPs with WZ structure [1,2,4]. The active ligand species captures the metal ion to control the nucleation and growth rate of NPs. Thus, the kinetics may predominantly contribute to the formation of a metastable phase such as WZ structure [2,3]. On the other hand, the ligand species selectively captures an indium ion to form a stable ligand–indium complex, which leads to the formation of Cu<sub>2-x</sub>S NPs. Several papers [10–13]

suggested that the formation of WZ CIS NPs was attributed to the pre-generation of Cu<sub>2</sub>S NPs. However, the detailed mechanism of phase selectivity of I–III–VI<sub>2</sub> NPs has not been understood.

Our investigation aims to understand the nature of polymorphism of CIS NPs. In the first part of this report, the thermolysis of Cu–In thiolate has been introduced into the synthesis of nearly monodispersed CIS NPs and examined with various organic compounds. In the latter part, we suggest the novel formation pathway of CIS NPs that consists of (i) the pre-generation of binary (Cu<sub>2-x</sub>S) NPs and (ii) the cation exchange reaction (or inter solid reaction). That is, we synthesized nearly monodispersed Cu<sub>2-x</sub>S NPs with various defect densities and crystalline structures [14] separately. Then, cation exchange reaction was conducted by aging of the Cu<sub>2-x</sub>S NPs in indium–thiolate solution. The polymorphism of CIS NPs is attributed to the structural variation of Cu<sub>2-x</sub>S seed NPs. This result provides a general strategy to control the crystalline structure of I–III–VI<sub>2</sub> NPs.

## 2. Experimental procedure

### 2.1. Synthesis procedure

All reagents used were as received. In a typical procedure, 0.4 mmol of copper (II) acetate (Cu(ace)<sub>2</sub>) and 0.4 mmol of indium (III) acetate (In(ace)<sub>3</sub>) were mixed with 2.24 ml of 1-dodecanethiol

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(DT; RSH) in ligand solution. After being degassed by Ar gas flushing for 1.8 ks, the mixture solution is heated up to 503 K. Except for acetates, chloride and thiolate were used as copper and indium sources. Experimental conditions are summarized in Table 1.

## 2.2. Cation exchange process

0.4 mmol (116.8 mg) of non-hydrous indium acetate and 10 mmol (2.46 ml) of DT were mixed with 15 ml of tri-*n*-octylamine (TOCA) in a round-bottom flask, which was then degassed by Ar gas flushing for 1.8 ks at 363 K. After flushing, Cu<sub>2-x</sub>S NPs dispersed in 5 ml of TOCA were added into In-DT complex solution and annealed for 1.8 ks at 473 K. The experimental procedure of Cu<sub>2-x</sub>S NPs synthesis has been already reported [14]. In this investigation, Cu<sub>1.8</sub>S (Cubic) and Cu<sub>2</sub>S (Hexagonal) NPs were used as seed NPs.

## 2.3. Purification process

After ethanol was added to the mixture solution at ambient temperature, dark brown precipitates were obtained. The precipitates were separated by centrifugation to remove excess reaction agents and then redispersed in hexane. This precipitate-redispersion procedure was repeated two times to purify the particles.

A drop of hexane solution with NPs was placed on a carbon-coated micro-grid for transmission electron microscope (TEM) observation, and examined with field emission TEM (Hitachi, HF-2000) operating at 200 kV with a point-to-point resolution power of 0.23 nm. The Cu<sub>2-x</sub>S and CIS NPs were characterized by X-ray diffraction (XRD, Mac Science, M18XCE) and a micro-Raman spectroscopy (Horiba Jobin Yvon Inc., LabRAM300) on sol samples dried onto a glass plates.

## 2.4. Optical properties measurement

The CIS NPs dispersed in hexane were placed in quartz cuvettes for linear (optical length = 10 mm) and nonlinear absorption measurement (1 mm). The linear absorption measurements of CIS NPs were performed in a UV-vis/NIR spectrometer (JASCO, V-570 equipped with PbS detector) with a scanning range from 200 to 2200 nm. Photoluminescence (PL) spectra and PL decay times were measured under excitation by a 510 nm (2.43 eV) line of a pulsed dye laser (repetition rate: 10 Hz, pulse duration: 10 ns). PL spectra

were recorded by a spectrograph equipped with a cooled CCD detector. In the PL decay time measurements, PL decay curves at the energies selected by a monochromator were recorded by a photomultiplier tube and a digital oscilloscope. The third-order nonlinear optical properties of NPs were examined by a standard open aperture Z-scan technique [15]. A laser beam from the above-mentioned pulsed dye laser (1.75 eV) was used in Z-scan measurements.

## 3. Results and discussion

### 3.1. Phase selective phenomena of CuInS<sub>2</sub>

Our previous paper reported that the metal thiolate served as the single source precursor for the synthesis of metal sulfide [1]. Copper and indium salt react with dodecanethiol molecules to form Cu–In thiolate. At temperature higher than 473 K, Cu–In thiolate is then decomposed into a CIS NP. Various organic compounds (Tri-*n*-octylamine (TOCA), Di-*n*-octylamine (DOCA), Oleylamine (OLA), Hexadecylamine (HDA), Di-*n*-octylether (OE), Hexadecane (HD) and Tri-*n*-octylphosphine (TOP)) were used as diluent to prepare CIS NPs. The diluents are classified into three types by the strength of interaction between a metal ion and the compound; Active ligand (L): DOCA, OLA, HDA and TOP; Weak ligand (L): TOCA; and Non-polar molecule: OE, HD. As shown in Table 1, the ligand and the metal source (MX<sub>m</sub>; M = Cu<sup>2+</sup> or In<sup>3+</sup>; X = RS<sup>-</sup>, ace<sup>-</sup> or Cl<sup>-</sup>) affected the shape and the crystalline structure of CIS NPs. Typical TEM images of CIS NPs are shown in Fig. 1a–c. CIS NPs obtained by thermolysis of Cu–In thiolate, exhibit three shapes such as a sphere (Fig. 1a), a hexagonal platelet (Fig. 1b) and a larva-like shape (Fig. 1c). CIS NPs having spherical shape with an average diameter of 2.0 nm are obtained from Cu and In-acetate (S2) in TOCA. As shown in Fig. 1b and c, DOCA and TOP lead to the morphological change of CIS NPs. XRD patterns indicate that CIS NPs take two crystalline structures; chalcopyrite (CP) and pseudo wurtzite (WZ). CIS NPs with a WZ structure mainly exhibit anisotropic shapes such as a larva-like and a hexagonal platelet shape. Crystalline structures, sizes and shapes of CIS NPs are summarized in Table 1.

Table 1 reveals that the thermolysis in the active ligand such as DOCA, OLA and TOP provides WZ-CIS NPs. On the other hand, CIS NPs obtained in weak ligand (TOCA) and non-polar molecule (OE, HD) take CP structure. Active ligand such as DOCA and TOP reacts with metal ion or metal thiolate to form metal ligand complex

**Table 1**  
Experimental conditions and results for Section 3.1.

Sample name	Cu source	In source	DT (mmol)	Solvent (20 ml)	Temp. (K)	Size (nm)	Crystalline structure <sup>a</sup>	Shape <sup>b</sup>
S1	Acetate	Acetate	10	TOCA	473	1.7	CP	Sphere
S2	Acetate	Acetate	10	TOCA	503	2	CP	Sphere
S3	Acetate	Acetate	10	TOCA	533	2.6	CP	Sphere
S4	Acetate	Acetate	5	TOCA	503	1.9	CP	Sphere
S5	Acetate	Acetate	20	TOCA	503	1.9	CP	Sphere
S6	Acetate	Acetate	10	DOCA	503	Large	WZ + CP	Larva + sphere
S7	Acetate	Acetate	10	OE	503	2.1	CP	Sphere
S8	Acetate	Acetate	10	TOP	503	Large	WZ	hp
S9	Acetate	Chloride	10	TOCA	503	Large	WZ	hp + sphere
S10	Acetate	Chloride	10	DOCA	503	Large	WZ	hp + sphere
S11	Thiolate	Thiolate	–	OE	503	1.7	CP	Sphere
S12	Thiolate	Thiolate	–	HD	503	1.7	CP	Sphere
S13	Thiolate	Thiolate	–	DT	503	1.8	CP	Sphere
S14	Thiolate	Thiolate	–	TOCA	503	1.8	CP	Sphere
S15	Thiolate	Thiolate	–	DOCA	503	2.3	CP	Sphere
S16	Thiolate	Thiolate	–	HDA	503	2.4	CP	Sphere
S17	Thiolate	Thiolate	–	OLA	503	6.9	WZ	Sphere

(S1–S10: [Cu] = [In] = 0.4 mmol, S11–S17: [Cu] = [In] = 1.0 mmol).

<sup>a</sup> CP: chalcopyrite phase, WZ: pseudo wurtzite phase.

<sup>b</sup> hp: Hexagonal platelet.

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