

The Synthesis of CuInS₂ Nanoparticles by a Simple Sonochemical Method

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CuInS₂ nanoparticles were synthesized by a simple sonochemical method; First, Cu nanoparticles were prepared from CuCl₂ in methanol solution by a one pot reaction through the sonochemistry under multibubble sonoluminescence (MBSL) conditions. Second, the resulting Cu nanoparticles were treated with InCl₃·4H₂O and CH₃CSNH₂ (thioacetamide) at the same MBSL conditions to synthesize In₂S₃-coated Cu nanoparticles in methanol solution. Then, they were transformed into CuInS₂ (CIS) nanoparticles of 20 ~ 40 nm size in diameter by thermal heating at 300 °C for 2 hr. The prepared CIS nanoparticles, of which band gap is 1.44 eV, were investigated by X-ray diffractometer, UV-Vis spectrophotometer, inductively coupled plasma spectrometer, and high resolution-transmission electron microscope.

Key Words: Cu nanoparticles, CuInS₂ (CIS) nanoparticles. Multibubble sonoluminescence conditions (MBSL)

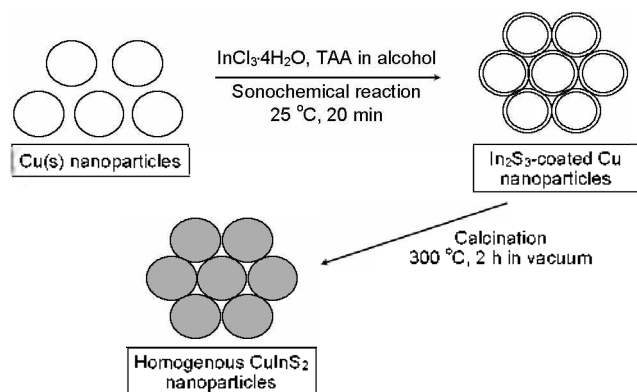
Introduction

The synthesis of well-known I-III-VI₂ ternary chalcogenide semiconductor materials has received intense interests to materials scientists and chemists because of their practical applications to photovoltaic cell. The ideal features¹ for solar cell materials include band gap in 1.1 ~ 1.7 eV range with direct band structures; readily available non-toxic materials; easy, reproducible deposition technique; suitability for large area production; good photovoltaic conversion efficiency; and long-term stability. Among them, CuInS₂ has been extensively studied since its band gap ($E_g = 1.5$ eV) is in optimum range for photovoltaic solar cell and the predicted theoretical efficiency of solar cells made with CuInS₂ as a non-toxic absorber layer is reported to be as high as 26%.² Various different morphologies of CuInS₂ of which band gap is about 1.5 eV have been prepared such as thin films,³ nanoparticles,⁴⁻⁵ nanorods,⁶⁻⁷ nanotube,⁸ nanowires,⁹ foam-like CuInS₂ nanocrystallites,¹⁰ and porous microspheres.¹¹ In fabricating the chalcogenide films, there were several techniques such as chemical vapor deposition,³ sputtering,^{7,12} spray pyrolysis,^{13,14} molecular beam deposition,¹⁵ and electrodeposition.^{16,17}

Recently, we reported that the sonochemistry under multibubble sonoluminescence conditions is a powerful method to synthesize various important nanomaterials such as CdS-coated TiO₂,¹⁸ Li₄Ti₅O₁₂,¹⁹ ZnO,²⁰ ZnS-coated TiO₂,²¹ PbS-coated TiO₂,²² and Ni-coated Al₂O₃,²³ nanoparticles with a core-shell structure under relatively very mild conditions.

The sonochemistry is an application of sonoluminescence (SL), which is a light emission phenomenon associated with the collapse of gas bubbles oscillating under an ultrasonic field.²⁴⁻²⁶ The estimated highest temperature and pressure in the liquid layer adjacent to the bubble were reported to be about 1000 °C and 500 bar,²⁰ respectively. Especially, in case of multibubble sonoluminescence (MBSL) conditions in our study, the reaction mixture was typically sonicated at 20 kHz and power of 220 W.²⁰ By these processes, homogeneous coating in nanoscale onto various nanoparticles was achieved as mentioned above. In general, it is well known that there were a large number of transient micro bubbles at the relatively low frequency of 20 kHz.²⁷⁻²⁸

In this study, CuInS₂ nanoparticles were synthesized through a sonochemical method for their possible application to the production of solar cell by a simple and low cost printing process. As shown in Scheme 1, first, Cu nanoparticles were prepared from CuCl₂ in methanol solution by sonochemistry under the multibubble sonoluminescence (MBSL) conditions. Second, In₂S₃-coated Cu nanoparticles were prepared using Cu nanoparticles, InCl₃·4H₂O, and CH₃CSNH₂ by the same sonochemical method as above. Finally, they were transformed into CuInS₂ nanoparticles by thermal heating at 300 °C for 2 h.



Scheme 1. Three steps method for CIS nanoparticles preparation by a sonochemical method.

Experimental Section

All reagents used were from Sigma-Aldrich Corp. All solvents were refluxed over molecular sieves 3 Å (pellets, 3.2 mm) to remove water molecules and then distilled before using them.

We used an experimental instruments described in our earlier research paper¹⁸⁻²² for the sonochemical system, consisting of a cylindrical quartz cell into which a 5 mm diameter titanium

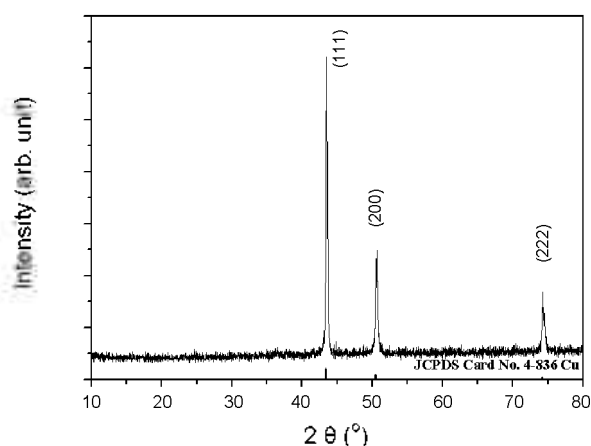


Figure 1. X-ray diffraction pattern of Cu nanoparticles.

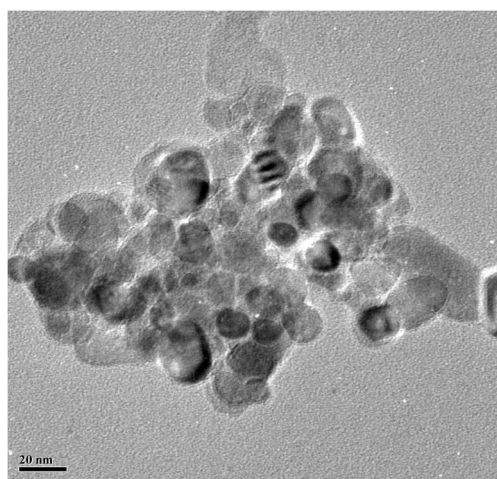


Figure 2. TEM image of Cu nanoparticles under MBSL conditions.

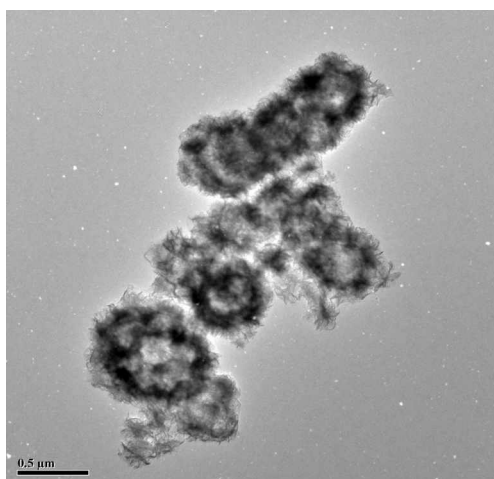


Figure 3. TEM image of In_2S_3 -coated Cu nanoparticles under MBSL conditions.

horn (Misonix XL2020, USA) is inserted. The sonochemical reaction system in this study was operated at 20 kHz and 220 W. The solution in the test cell was kept at 1.4 atm under argon gas and the temperature of the solution inside the quartz cell was

kept to around 25 °C by a circulating water bath.

Preparation of Cu nanoparticles. Cu nanoparticles were prepared from CuCl_2 in methanol solutions through the aforementioned sonochemical treatment: in a typical case, CuCl_2 (Aldrich: 0.1386 g, 1 mmol) in MeOH (12 mL) was sonicated under MBSL conditions for 5 ~ 20 min. Resulting Cu nanoparticles (yield: 47.3%) were washed with deionized-water, alcohol and acetone in order and dried in a vacuum oven at 60 °C for 12 h, and were examined by a Scintag XDS-2000 X-ray diffractometer and high resolution-transmission electron microscope (HR-TEM; JEOL JEM-3010), using samples prepared on 50 mesh TEM grid after dispersed in methanol solution at accelerating voltage of 300 kV.

In_2S_3 -coated Cu nanoparticles. The prepared Cu nanoparticles were coated with In_2S_3 by the same sonochemical treatment as above, using Cu nanoparticles, $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$, and CH_3CSNH_2 (thioacetamide) in methanol solution. In order to find proper coating depth of In_2S_3 for the preparation of CuInS_2 nanoparticles, several sonochemical reactions with different reactant ratios among Cu nanoparticles, $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$, and CH_3CSNH_2 were tried through the sonication at the aforementioned conditions for 20 min in methyl alcohol (13 mL) solutions. The best result, leading to the stoichiometric CuInS_2 nanoparticles, was obtained when 0.2 mmol Cu nanoparticles (0.0573 g) were sonicated with 1 mmol $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ (0.9069 g) and 1.5 mmol CH_3CSNH_2 (0.3485 g) in 13 mL methanol. The color of In_2S_3 -coated nanoparticles was bright brown and the resulting particles were washed with DI-water, alcohol, acetone in order and dried at vacuum oven at 60 °C for 12 h.

CuInS_2 nanoparticles. CuInS_2 nanoparticles were prepared by heating the In_2S_3 -coated Cu nanoparticles at 300 °C for 2 h in vacuum. The resulting In_2S_3 -coated Cu and CuInS_2 nanoparticles were characterized by various instruments, such as X-ray diffractometer, UV-Vis spectrophotometer (Scinco S-3100), high resolution-transmission electron microscope (HR-TEM; JEOL JEM-3010). The atomic ratio was examined by inductively coupled plasma spectrometer (ICP; Jobin Yvon JY-Ultima-2).

Results and Discussion

As shown in Figure 1 and 2, Cu nanoparticles were easily prepared by a simple one pot sonochemical reaction, which is environmentally benign. The XRD pattern of the Cu nanoparticles prepared with 20 min sonication indicates that they are in a cubic phase²⁹ without any impurity such as copper oxide with most intense peaks at $2\theta = 43.3^\circ$, 50.47° , and 74.2° , corresponding to (111), (200), and (222) planes. Their size was found to be in 20 ~ 40 nm range on the basis of TEM image in Fig. 2. It is noteworthy that the Cu nanoparticle size can be simply controlled by adjusting the sonication time under the described MBSL conditions: the average Cu nanoparticle size increases from 7 nm to 50 nm in diameter as the sonication time increases from 5 min to 25 min. In this experiment, methyl alcohol functions as both reducing agent and reaction medium in the above described sonochemical reaction.

Fig. 3 shows the TEM image of In_2S_3 -coated Cu nanoparticles and its XRD pattern of indicates that the In_2S_3 can be assumed to be in a cubic phase³⁰ with the characteristic intense peaks at $2\theta = 47.9^\circ$, 43.8° , and 27.5° corresponding to (440), (511), and

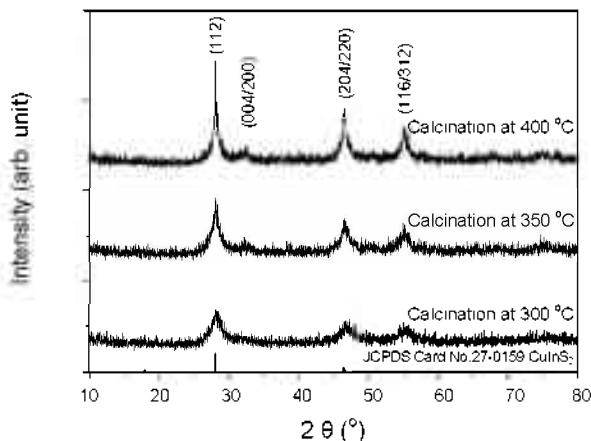


Figure 4. X-ray diffraction patterns of CuInS₂ nanoparticles after calcination at different temperatures at (a) 300 °C, (b) 350 °C, (c) 400 °C.

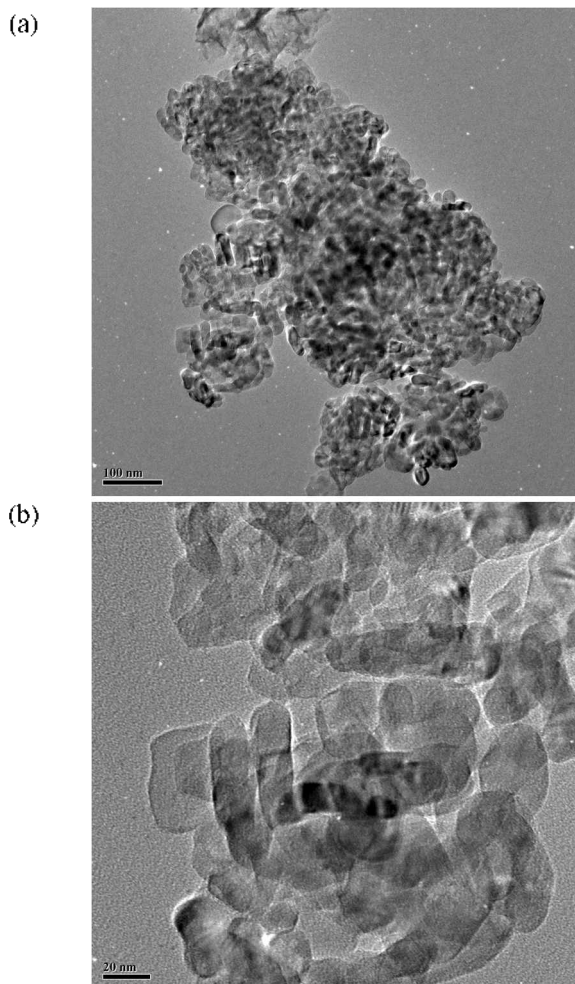


Figure 5. TEM image of (a) CIS nanoparticles under MBSL conditions after calcination at 300 °C, (b) its HR-TEM image.

(311) planes, though the peaks were quite weak in intensity and very broad since the In₂S₃ coating is in nanoscale.

After calcinations of the In₂S₃-coated Cu nanoparticles at 300 °C for 2 h, they were transformed into CuInS₂ (CIS) nanoparticles which are in a tetragonal phase³¹ with the most intense

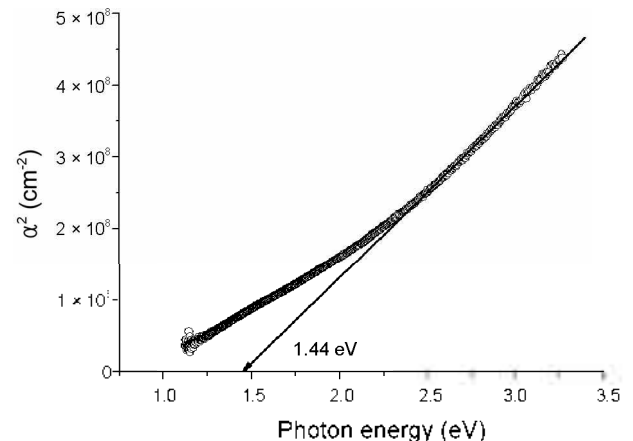


Figure 6. Typical plot of α^2 vs. band gap of CIS nanoparticles fabricated under MBSL conditions (α : absorption coefficient).

peaks $2\theta = 27.8^\circ$, 46.2° , and 55.1° corresponding to (112), (204), and (312) planes, as shown in Figure 4. The mean crystallite size diameter (D) of nanoparticles can be calculated on the base of XRD spectra by the Scherrer's formula.³²

$$D = \frac{0.9\lambda}{B \cdot \cos \theta_B} \quad (1)$$

where λ is the X-ray wavelength, B the full-width at half maximum and θ_B represents the diffraction angle at a certain crystal plane. The calculated sizes are about 35 nm in diameter at the calcinations temperature of 300 °C for 2 h. Figure 5 shows that the CIS nanoparticle size is in 20 ~ 40 nm range.

As shown in Figure 6, the band gap of the CIS nanoparticles was found about 1.44 eV on the basis of UV-Vis spectrophotonic data and the equation (2):

$$(ah\nu)^2 = (E_g \times a)^2 \quad (2)$$

where E_g (eV) is the $\frac{1239.841223}{\lambda}$; λ is the wavelength (nm) from vis-near IR band, is the energy of a photon; h is the Planck's constant, a is the absorption coefficient $a = \frac{A}{t}$; A = absorbance spectrum (vis-near IR), $t = 0.0001$ (1000 nm). That value was in optimal band gap range for the photovoltaic solar cells,¹ but was a little bit higher than that³³ (1.41 eV) of CIS thin films obtained by MOCVD method. According to inductively coupled plasma spectrometer (ICP) results, the ratio of Cu to In to S was 1.00 : 1.17 : 2.17.

Conclusions

In this study, the CuInS₂ nanoparticles were synthesized through a sonochemical method: First, Cu nanoparticles were prepared from CuCl₂ in methanol solution by sonochemistry under the multibubble sonoluminescence (MBSL) conditions. Second, resulting Cu nanoparticles were coated with In₂S₃ by reacting Cu nanoparticles with InCl₃·4H₂O and CH₃CSNH₂ in methanol solution by the same sonochemical method as above.

Finally, the In_2S_3 -coated Cu nanoparticles were transformed into CuInS_2 nanoparticles by heating them at 300 °C for 2 h. Thus, our synthesis process for CuInS_2 nanoparticles preparation was found relatively very mild and simple in comparison to other methods to prepare CuInS_2 nanoparticles such as solvent thermolysis,^{2,4,34-40} hydrothermal route,^{5,7,41} and microwave irradiation.⁴²

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