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# Rapid Synthesis and Characterization of $CuInS_2$ Prepared using Microwave-assisted Heating

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**Abstract.** In this work, the $CuInS_2$ nanoparticles are successfully synthesized by microwave-assisted heating technique and further calcined at 400 $^oC$. The morphological, structural, and optical properties of the synthesized $CuInS_2$ nanoparticles are investigated by scanning electron microscope (SEM), X-ray diffraction (XRD), Raman scattering, and transmittance measurement, respectively. The SEM image shows the clear particle shape of the calcined $CuInS_2$ nanoparticles. After calcination treatment, the fundamental (112) peak of the XRD spectrum and a broad Raman peak mixed with chalcopyrite and CuAu structures support the improved crystallinity of the calcined $CuInS_2$ nanoparticles.

## Introduction

Copper indium disulphide ($CuInS_2$) material belonging to I–III–VI semiconductor is a promising material for high efficiency solar cell fabrication. $CuInS_2$ material has a direct band gap of 1.5 eV, which matches very well with the solar spectrum. It has been known that $CuInS_2$ material has three polytypes, including the chalcopyrite (CH), CuAu (CA), and CuPt structures. It has been observed that the CH and CA phases usually coexist in the grown $CuInS_2$ [1-2].

Up to now, $CuInS_2$ materials have been produced by several different methods, such as sources molecular beam epitaxy [3], sulphurisation of metallic precursor [4], reactive sputtering [5]. It is important to develop better structural, electronic, and optical properties of $CuInS_2$ ternary alloys for the purpose of device applications. In this work, we report on the use of microwave-assisted heating for growing $CuInS_2$ nanoparticles (NPs). We present the feasibility of controlling morphologies of $CuInS_2$ NPs under calcination treatment confirmed by scanning electron microscopy (SEM). In addition, the crystalline quality and optical properties of the calcined $CuInS_2$ NPs are investigated by using x-ray diffraction (XRD), Raman scattering and transmittance spectroscopy.

## Experimental Procedure

$CuInS_2$ NPs were prepared by microwave-assisted synthesis. First, a precursor solution was prepared by stirring a mixture with 1:1:3 molar ratio of $CuCl_2$ to $InCl_3$ to $Na_2S$ based on 0.03 M in ethanol to obtain a well-dissolved solution. The prepared solution was then placed into a microwave oven and heated from room temperature up to 60 °C with magnetic stirring within 0.5 hour. The obtained powder was then cleansed twice with alcohol and finally dried at room temperature. The as-synthesized $CuInS_2$ NPs were further calcined in Ar atmosphere at the temperature of 400 $^oC$ for 2 hours. The $CuInS_2$ NPs mixed with PEG were deposited on corning glass using doctor blade method.

The X-ray diffraction (XRD) spectrometer (Shimadzu XRD-6000) with a CuKα line of 1.5405 Å was used to study the crystal phases in the $CuInS_2$ NPs. The Raman scattering measurements were

carried out by using the Renishaw System (inVia Raman microscope) at room temperature. Raman spectra were excited with the 514.5 nm line of an $Ar^+$ laser at an incident power of 10 mW. The SEM images were taken on a JEOL-JSM7001F to observe the morphology of the as-synthesized and calcined $CuInS_2$ NPs. The absorption spectra were taken from transmittance measurement set up by monochromatic light from the Oriel 1000 W halogen light source. The transmitted light passed through the sample and was then to Si detector. The signal was measured by a lock-in amplifier and recorded by a computer.

**Results and Discussion**

The morphology and particle size of the as-synthesized and calcined $CuInS_2$ NPs were studied by SEM. As shown in Fig. 1(a), the SEM image of the as-synthesized $CuInS_2$ NPs showed particulates covered by a large cloud of organic complexes. After the calcination temperature of 400 °C, the SEM image as presented in Fig. 1(b) shows a clear particulate formation of the calcined $CuInS_2$ NPs.

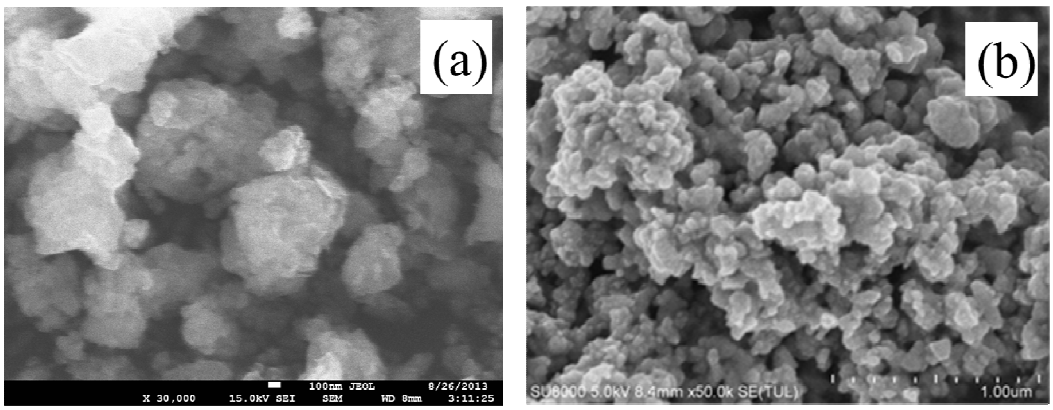


Figure 1 The SEM images of the (a) as-synthesized, and (b) calcined $CuInS_2$ NPs

Figure 2 shows the XRD patterns measured in the 2θ (degree) range of 10–80 to examine the crystal structure as well as the chemical composition. Referring to the JCPDS card No. 27-0159, 06-0464, and 26-1116, the significant diffraction peaks corresponded to the $CuInS_2$, CuS, and $Cu_2S$ are indicated, respectively. Among the XRD patterns, it has been known that the (112) diffraction peak is directly related to the crystal quality of $CuInS_2$ materials [6]. Therefore, the intensity of the (112) diffraction peak being identified clearly after annealing at 400 °C indicates the improved crystallinity of $CuInS_2$ NPs.

In addition, the particle size ($D$) of the calcined $CuInS_2$ NPs can be determined by using the Scherrer's equation for the full width at half-maximum (FWHM) of the (112) peak. The Scherrer's equation is $D = 0.9\lambda / B\cos\theta$, where $\lambda$, $\theta$, and $B$ are the X-ray wavelength, Bragg diffraction angle, and FWHM in radians, respectively [7]. The calculated average particle size is about 12.8 nm for the sample annealing at 400 °C.

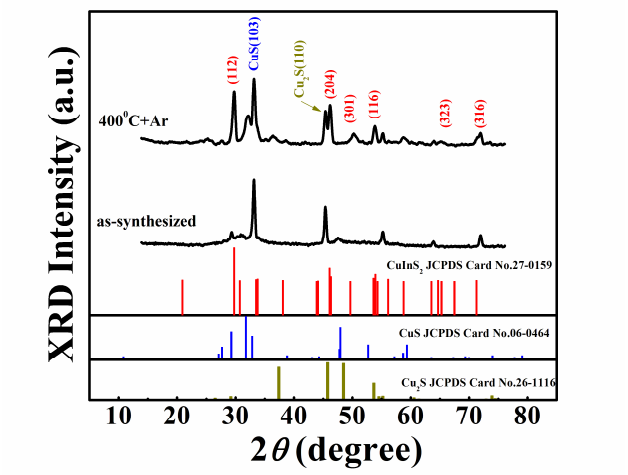


Figure 2 XRD patterns of the as-synthesized and calcined $CuInS_2$ NPs

Raman scattering is an effective tool for the determination of structural quality and phase purity. The Raman spectrum are measured in the range of 200–400 $cm^{-1}$ and shown in Fig. 3. The Raman signals of the as-synthesized $CuInS_2$ NPs cannot be clarified, but that of the calcined $CuInS_2$ NPs would be exhibited clearly. According to Ref. 8, two weaker peaks located at about 240 and 340 $cm^{-1}$ are attributed to the $E^3_{LO}$ and $E^1_{LO}/B^1_{2LO}$ modes, respectively. On the other hand, a significant signal with a broad range of 280–320 $cm^{-1}$ can be observed as a mixture of two peaks. The two peaks at about 291 and 305 $cm^{-1}$ are assigned to the CH and CA mode, respectively [9-10]. The Raman spectra indicate that the significant CH or CA structure of $CuInS_2$ NPs could be presented by the annealing treatment.

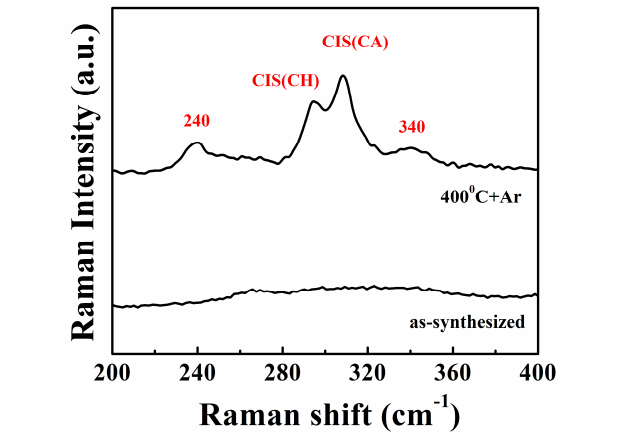


Figure 3 Raman spectra of the as-synthesized and calcined $CuInS_2$ NPs

Energy bandgap of $CuInS_2$ NPs is investigated by the absorption spectra transferred from transmittance measurement. To estimate the energy bandgap from the absorption spectra, the Tauc relation is used: [11]

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \tag{1}$$

where $h\nu$ is the photon energy, $\alpha$ the absorption coefficient, $E_g$ the bandgap, $A$ the constant, and $n$ = 1/2 for direct bandgap material, and $n = 2$ for indirect bandgap. To obtain the energy bandgap from the absorption spectra, a graph $(\alpha h\nu)^n$ versus $h\nu$ is plotted [12]. The extrapolation of the straight line to $(\alpha h\nu)^n = 0$ gives the value of the energy bandgap.

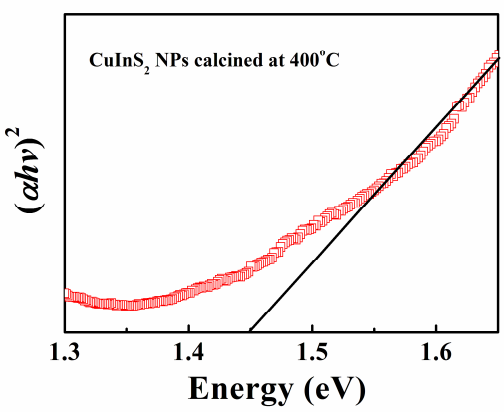


Figure 4 Direct energy bandgap determination of the calcined $CuInS_2$ NPs by the absorption spectra

Figure 4 shows a plot between $(\alpha h\nu)^2$ versus $h\nu$ for the calcined $CuInS_2$ NPs due to its direct bandgap. The extrapolation of straight line to $(\alpha h\nu)^2 = 0$ can estimate the value of the direct bandgap of the $CuInS_2$ NPs calcined at 400 °C to be about 1.45 eV, which is considerable for photovoltaic applications.

## Summary

The synthesized $CuInS_2$ NPs prepared by the microwave-assisted heating technique were calcined at the temperature of 400 °C in Ar atmosphere. Then, the investigations of the SEM image and the (112) XRD peak of the calcined $CuInS_2$ NPs have indicated that the annealing treatment would improve the crystallinity of the synthesized $CuInS_2$ NPs. It was also observed that the calcined $CuInS_2$ NPs show a broad Raman peak consisted of CH and CA modes. Furthermore, the value of the direct bandgap for the calcined $CuInS_2$ NPs can be obtained to be about 1.45 eV from the absorption spectra.

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