Synthesis of oleic acid-capped CuInS₂ nanocrystals from bimetallic hydroxide precursor

Seonho Jung, Ji-Hyun Cha, Duk-Young Jung *
Department of Chemistry, Sungkyunkwan Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon 440-746, Republic of Korea

A R T I C L E   I N F O
Article history:
Received 21 December 2015
Accepted 13 February 2016
Available online 17 February 2016

Keywords:
Photovoltaics
Nanocrystals
Copper indium sulfide
Oleic acid
Bimetallic precursor

A B S T R A C T
CuInS₂ colloidal nanocrystals were synthesized via a facile solution-processed method, using a CuIn(OH)₅ precursor. The Cu–In metal hydroxide precursor was prepared by co-precipitation in aqueous solution: an aqueous NaOH solution was reacted with a metal cation solution containing Cu²⁺ and In³⁺ ions at room temperature. Oleic acid was added as a surfactant and bis(trimethyldisilyl)sulfide was injected to provide a sulfur source for the formation of CuInS₂ nanocrystals. The CuInS₂ colloidal nanocrystals had mixed crystal structures of zincblende and wurtzite, confirmed by XRD and TEM. The CuInS₂ nanoparticles were of average size 5.6 nm and had a 1:1:2 chemical composition. Paste of the as-prepared CuInS₂ nanocrystals were coated as a thin film absorber layer for photovoltaic cells by doctor blading, yielding cell efficiency of 1.26%.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Colloidal nanocrystals (NCs) of semiconducting compounds have been studied for their novel optical properties and potential applications [1], such as in solar energy conversion, photocatalysis, drug delivery, and photodetection. NCs also have the fascinating advantage of allowing chemical solution-processing [2], such as in the printed fabrication of thin film photovoltaic (PV) device [3]. CuInS₂ (CIS) is a I-III-VI₂ semiconductor that has shown a high extinction coefficient and a suitable bandgap for use as a solar-harvesting layer in PV cells [4]. The CIS NCs have been synthesized by hot-injection [5], solvothermal [6], and heat-up methods [7]. In these synthetic processes, there are difficulties in controlling the relative reactivities of the two metal precursors to avoid undesired side-products, and to adjust ratios of copper to indium because the electrical and optical properties of CIS NCs depend strongly on their stoichiometry [3,8,9]. Herein we present a strategy to synthesize a CIS NCs by sulfurization of CuIn(OH)₅ precursor; the use of this precursor avoided the formation of side products such as CuS, and the resulting CIS NCs had molar Cu:In:S compositions of 1:1:2.

To fabricate the CIS NCs, oleic acid was used as a surfactant for ligand passivation [10] to enhance electrical properties in the fabrication of thin film device. As far as we know, there have been no reports so far of CIS NCs capped by oleic acid ligands. Although oleylamine or thiol are typical capping agents used to stabilize CIS nanocrystals [2,11], which form stronger interactions with copper ions (which are soft Lewis bases) than oleic acid (which is a hard Lewis acid) [3,12]. As-synthesized CIS NCs form stable colloidal dispersions in non-polar solvents such as hexane, chloroform, and toluene for 180 days or more.

In this study, we demonstrate the synthesis of stable oleic acid-capped CIS NCs by means of facile solution processing and low-cost CIS deposition, using CIS NCs-based ink as a light-absorbing layer of PV cells, annealed in a sulfurization process. The oleic-capped CIS NC ink was coated simply onto a molybdenum substrate by means of doctor blading, and thin film PV cells with typical substrate-type configuration were fabricated.

2. Experimental details

2.1. Materials

Copper(II) chloride, indium(III) chloride, sodium hydroxide, ammonium sulfide, oleic acid (OA), oleylamine (OLAM), 1-octadecene, bis(trimethylsilyl) sulfide, formamide, cadmium sulfate, thiourea, ammonium hydroxide, and chloroform were purchased from Sigma-Aldrich. Hexane, ethanol, 2-propanol, and acetone were obtained from Samchun Chemical.

2.2. CuIn(OH)₅ precursor synthesis

To prepare the CuIn(OH)₅ precursor, 1.344 g of CuCl₂, 2.211 g of InCl₃, and 200 mL of deionized water were poured into a flask and stirred for 1 h (Fig. 1a). A NaOH solution was prepared by adding 8 g of NaOH to 100 mL of deionized water, and was added to the CuIn chloride solution until its pH reached 8.0. This solution was aged for 2 h, the supernatant layer was removed, and the precipitate was washed.
with a mixture of ethanol and deionized water three times, yielding CuIn(OH)₅ precursor as powder.

2.3. CuInS₂ nanocrystal synthesis

CuIn(OH)₅ powder of 0.265 g was added into a 3-neck round bottom flask, followed by addition of 20 mL of OA and 10 mL of OLAM under nitrogen atmosphere. The mixture was heated to 150 °C for 30 min under nitrogen atmosphere until the powder completely dissolved. The solution was then cooled to 120 °C and dehydrated by placing it under vacuum conditions for 30 min. Then, the solution was reheated to 200 °C, yielding yellow-colored CuIn–OA solution. Bis(trimethylsilyl)sulfide/1-octadecence solution was prepared by dissolving 230 μL of TMS in 5.5 mL of ODE; ODE was degassed under vacuum for 1 h before use. 5 mL of TMS-ODE solution was injected rapidly into the CuIn–OA solution at 200 °C and held at this temperature for 5 min to allow the growth of CIS NCs (Fig. 1b). The solution was cooled to room temperature, and then acetone was added to the flask to precipitate crude CIS nanocrystals. The CIS NCs were centrifuged and washed in a 1:1 mixture of hexane and ethanol; this was done twice. The resulting oleic acid-capped CIS NCs remained well-dispersed in non-polar solvent for at least six months.

2.4. CuInS₂ PV device fabrication

The as-synthesized CIS colloidal solution was used as the absorber for solar cells (Fig. 1c). PV device was fabricated in the following configuration: glass/Mo/CIS/CdS/i-ZnO/n-ZnO/Ag. To coat a dense film of CIS onto a Mo layer on a glass substrate (20 mm × 20 mm), the Mo layer was first washed with 2-propanol and acetone. The solution of the OA-capped CIS NCs in chloroform was coated by doctor blading, and the resulting CIS-coated substrate was dried on a hot plate for 1 h at 330 °C. This substrate was rapidly annealed for 1 h at 550 °C under H₂S gas. CdS buffer layer was added by means of a chemical bath deposition method; the substrate was immersed in an aqueous solution of CdSO₄ (1.161 g, 50 mL), SC(NH₂)₂ (2.88 g, 25 mL), and 28–30%
NH₄OH (65 mL) for 7 min at 70 °C [13,14]. Top layers of i-ZnO/n-ZnO were deposited by radio frequency sputtering with their targets in Ar atmosphere, followed by deposition of silver electrode by thermal evaporation method.

2.5. Ligand removal

OA-capped CIS colloidal NCs were dispersed in hexane, a nonpolar solvent which is the supernatant (Fig. 2). Inorganic (NH₄)₂S reagents were prepared in formamide, a polar solvent immiscible with the supernatant. To exchange organic ligands with S²⁻ ions, 20 mL of CIS solution (5 mg/mL) was stirred with 20 mL of (NH₄)₂S solution (60 μL/mL) for 12 h until phase transfer was completed. This was easily monitored by color changes: the hexane changed from black to colorless and formamide changed from yellow to black as the CIS NCs were transferred to the formamide. Then, the hexane supernatant was discarded and the formamide colloidal solution was separated out followed by washing with ethanol/hexane three times to remove any remaining nonpolar organic species. The surfactant-free CIS NCs were dispersed in polar solvent for 24 h.

3. Results and discussion

OA-capped CIS NCs were synthesized from a bimetallic hydroxide precursor in the mixture of OA and OLAM solvents. The CuIn(OH)₅ metal hydroxide precursor vigorously reacted with TMS to give dark brown-colored CIS NCs. The CIS NCs were well dispersed, without inter-particle aggregation, and had the average diameter of 5.6(9) nm (Fig. 3a). The CIS NCs were spherical and had the inter-particle spacing of 2.1 nm (Fig. 3b).

The crystal structure of the prepared CIS NCs was investigated by fast Fourier transform (FFT) method (carried out using Gatan Digital Micrograph program), transforming the data shown in Fig. 3b. The resulting FFT images showed hexagonal lattice fringe of the (010) and (110) reflections of the wurtzite structure (space group: P6₃mc, hexagonal unit cell), observed at 3.40 and 1.94 Å, respectively (Fig. 3c, d). The FFT image in Fig. 3d could be also indexed to the (111) plane of the zincblende structure (space group: F-43 m, cubic unit cell), which has the basal spacing of 3.19 Å. The as-synthesized CIS NCs were thus considered to comprise mixed phases of wurtzite and zincblende, supported by subsequent XRD analysis (vide infra).

Typically, the solution process formed the metastable CIS NCs of wurtzite and zincblende phases having copper and indium cations randomly distributed in the metal sites [15,16]. The crystal structure of CIS NCs can be altered by the reaction environment, including the capping agents, starting materials, solvent pH, and reaction kinetics [17–19], supporting the conclusion that mixed-phase CIS NCs were produced in the present study. The elemental maps of the CIS NCs showed that the Cu, In, and S elements were homogeneously distributed (Fig. 3e), indicating that the use of the bimetallic hydroxide precursor yielded high-purity ternary CIS NCs.

FT-IR analysis was carried out to determine whether the OA surfactant encapsulated the CIS NCs (Fig. 4). The following bands were observed: a band at 2960 cm⁻¹ corresponding to stretching vibration of CH₃; bands at 2923 and 2854 cm⁻¹ corresponding to antisymmetric and symmetric stretching of C–H; the band around 1730 cm⁻¹ corresponding to stretching vibration of C = O of carboxylic acid; a band at 1463 cm⁻¹ corresponding to –CH₂ deformation; and a band at 1265 cm⁻¹ corresponding to C–O stretching peak, with the same peak as that of OA (Fig. 4b) [20–22]. The presence of OA was investigated further by means of ligand removal treatment with

**Table 1**

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Cu:In of CuIn(OH)₅</th>
<th>Cu:In:S of CuInS₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPMA</td>
<td>0.99:1.00</td>
<td>1.17:1.00:2.17</td>
</tr>
<tr>
<td>ICP</td>
<td>1.01:1.00</td>
<td>0.92:1.00:2.08</td>
</tr>
<tr>
<td>EDS</td>
<td>0.93:1.00</td>
<td>0.92:1.00:1.93</td>
</tr>
</tbody>
</table>

Fig. 4. FT-IR spectra of (a) CIS NCs covered by OA, (b) OA only, (c) CuIn(OH)₅ precursor, and (d) surfactant-free CIS NC.
(NH₄)₂S solution and ligand exchange by means of a phase transfer method [23,24]. After this treatment, the characteristic peaks of the OA ligand were no longer present in the FT-IR spectrum, indicating that OA surfactants were completely exchanged to S²⁻ ions, forming soluble (NH₄)OA that was removed by the filtration [24]. FT-IR spectrum of CuIn(OH)₅ showed bands at 3455 cm⁻¹ (O–H stretching), 1622 cm⁻¹ (H₂O bending), and 841 cm⁻¹ (M–OH bending) [25,26]. The peaks corresponding to H₂O molecules were observed which were absent from the spectrum of OA-covered CIS NCs (Fig. 4a) indicating that H₂O molecules were removed during the synthesis of CIS NCs.

Table 1 lists the chemical compositions of the CuIn(OH)₅ precursors and the prepared CIS NCs. Quantitative analyses of CIS NCs by means of EPMA (electron probe micro analyzer), ICP (inductively coupled plasma), and EDS (energy-dispersive X-ray spectroscopy) indicated that they had Cu:In:S composition ratios of 1:1:2, in accord with the stoichiometry of CIS semiconductor. In the present synthesis, the 1:1 Cu:In composition ratio of the CuIn(OH)₅ precursor remained intact after the hot-injection reaction to form CIS NCs.

The experimental XRD patterns of as-synthesized CIS NCs (Fig. 5a) were indexed by comparing them to simulated XRD patterns of the zincblende, wurtzite, and chalcopyrite structures [16,27,28]. In the zincblende and wurtzite structures of CIS, the indium and copper are randomly distributed in the cation sites [29]. As shown by the XRD data, the crystal structure of CIS NCs was mixed-phase of zincblende and wurtzite. To calculate the lattice parameter of the mixed-phase CIS NCs, we investigated the crystal growth of zincblende and wurtzite-type CIS NCs by controlling the reaction time of the CuIn–OA solution; XRD analysis of the resulting CIS NCs clearly showed single phases of zincblende and wurtzite-type CIS NCs (Fig. 6) [30]. The lattice parameter of zincblende-type CIS NCs was a = 5.524 Å, close to reference data. Those of wurtzite-type CIS were a = 3.899 Å and c = 6.461 Å. The average size of CIS NCs was estimated to be 6 nm by using the Scherrer equation [31], close to the 5.6 nm from TEM images. Remarkably, after annealing at 550 °C for 1 h, the CIS NCs had four times improved crystallinity compared with the as-synthesized CIS NCs. However, it was not possible to determine the crystal structure, zincblende and chalcopyrite phases based on XRD measurements.
Raman spectral data supported the identification of the CIS NCs’ crystal structure and the determination of the presence of organic surfactant (Fig. 7). Generally, the most prominent bands of the CIS compound are found in the range of 255–360 cm\(^{-1}\) [28]. The main peak of as-prepared CIS NCs solely appeared at 303 cm\(^{-1}\); this peak is attributed to the sulfur-related vibrational mode of CIS compounds derived from the zincblende structure [32]. The B\(_2\) mode of In–S antiphase vibration of CIS was observed at 260 cm\(^{-1}\), originating from the wurtzite structure [32,33]. The peak at 347 cm\(^{-1}\) originated from the E\(_{\text{LO}}\) and B\(_{\text{2}}\)\(_{\text{LO}}\) modes of Cu–S; this peak is considered to represent the amount of disordered structure of CIS [34,35]. Metal ions of CIS sample occupy a random position in comparison with that of ordered chalcopyrite-type CIS NCs [28,35], resulting in the mixed-phase of zincblende and wurtzite structures. After rapid thermal annealing treatment for 1 h at 550 °C, the peak of the A\(_1\) mode of chalcopyrite-type CIS appeared at 297 cm\(^{-1}\) (Fig. 7a) and the D, G carbon peaks decreased (Fig. 8) [32]. The lattice parameters of chalcopyrite-type CIS were estimated as \(a = 5.514\) Å and \(c = 11.097\) Å, demonstrating that the mixed crystal structures of CIS were transformed to the chalcopyrite phase [33,36] during the removal of the organic ligands of CIS by annealing.

Since copper ions are much reactive than indium ions, the CuxS phase has been often detected in the Raman spectra when carboxylic acids were used in the synthesis of CIS NCs [36]. The control of the chemical composition is difficult because carboxylic acids are hard Lewis acid ligands whereas copper ions are soft Lewis bases. To balance the reactivities of the copper and indium metal cations, alkane thiol has been applied, but in most cases, CuxS species are detected as a side product [37]. In the present study, we successfully synthesized OA-capped CIS NCs from CuIn(OH)\(_5\) bimetallic precursor, without forming a CuxS phase, by using the two stabilizers, OA and OLAM.

UV–Vis absorption spectra of the as-synthesized CIS NCs were collected (Fig. 9) to estimate the optical bandgap (\(E_g\)) of the as-prepared CIS NCs by plotting \((ahv)^2\) [38]. The bandgap of the as-synthesized CIS NCs was about 2.5 eV. As the particle size decreases, the CIS bandgap can be tuned from 1.4 to 3.3 eV due to quantum confinement [3,38]. After annealing, CIS NCs formed bulk crystalline CIS of bandgap 1.45 eV, close to the direct bandgap of CIS bulk crystals [3]. SEM images and electrical characteristics of a CIS thin film PV device under AM1.5 illumination (100 mW/cm\(^2\)) are shown in Fig. 10. CIS thin film PV devices of the configuration of glass/Mo/CIS/CdS/i-ZnO/n-ZnO/metal electrode [39,40] were fabricated (Fig. 10a, b). The CIS and CdS layers were coated by doctor-blading and chemical bath deposition; their thicknesses were 1 µm and 80 nm, respectively. The sputtered i-ZnO/n-ZnO layer was 950 nm of thickness.

The \(J–V\) characteristics, transformed from an \(I–V\) curve, indicated that the device responded as a pn-diode due to the \(pn\)-junction between the CIS and CdS layer, and that when the device was irradiated, it yielded photocurrent (Fig. 10c). The square area of each cell was 0.24 cm\(^2\) excluding electrode area. The low short-circuit current (\(J_{sc}\)) value of 5.24 mA/cm\(^2\) resulted from poor charge transport in CIS absorption layer; the device showed fill factor (FF) of 0.508 and open-circuit voltage (\(V_{oc}\)) of 0.47 V. The low \(J_{sc}\) value may have been caused by organic residue remaining after rapid thermal annealing treatment (Fig. 8). The cell efficiency of 1.26% was obtained from a device with a

---

**Fig. 8.** Raman spectra (Raman shift: 200–2000 cm\(^{-1}\)) of CIS thin film surface (a) before and (b) after annealing.

**Fig. 9.** Absorbance spectra of CIS NCs (a) before and (b) after annealing. Insets: Tau plots transformed to calculate the absorption edges of (a) 2.5 eV and (b) 1.45 eV bandgap.

**Fig. 10.** (a) Top-view and cross-sectional SEM images of the as-prepared CIS thin film coated by doctor blading; (b) schematic CIS solar cell device fabricated in the present work; (c) efficiency calculated from \(J–V\) characteristics.
CIS layer 1 nm thick as an absorber. However, the photovoltaic efficiency in this device could be improved by optimizing the thickness of layers, the coating density, the chemical composition of the CIS, and so on.

4. Conclusion

A facile synthesis of Culn(OH)3 powder in aqueous solution was applied to fabricate CuS-free CIS NCs in a thin film process including the use of OA and OLAM stabilizers. This bimetallic hydroxide precursor provided stoichiometric metal compositions of copper and indium. The CIS NCs were covered by OA surfactants and consisted of a mixed crystal structure of zincblende and wurtzite, which transformed to the chalcopyrite phase after heat treatment. The OA-capped CIS NCs were useful for the low-cost deposition of a CIS absorption layer in thin film solar cells. The OA surfactants of CIS NC can be easily removed or replaced with other ligands for use in various applications.

Acknowledgment

This work was supported by National Core Research Center (NRF-2009-0083540), the Basic Science Research Programs (NRF-2013R1A1A2007482), and the Fusion Research Program for Green Technologies (NRF-2012M3C1A0 48862) through the National Research Foundation of Korea.

References