



# Synthesis of oleic acid-capped CuInS<sub>2</sub> nanocrystals from bimetallic hydroxide precursor



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## ABSTRACT

CuInS<sub>2</sub> colloidal nanocrystals were synthesized via a facile solution-processed method, using a CuIn(OH)<sub>5</sub> 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 Cu<sup>2+</sup> and In<sup>3+</sup> ions at room temperature. Oleic acid was added as a surfactant and bis(trimethylsilyl)sulfide was injected to provide a sulfur source for the formation of CuInS<sub>2</sub> nanocrystals. The CuInS<sub>2</sub> colloidal nanocrystals had mixed crystal structures of zincblende and wurtzite, confirmed by XRD and TEM. The CuInS<sub>2</sub> nanoparticles were of average size 5.6 nm and had a 1:1:2 chemical composition. Paste of the as-prepared CuInS<sub>2</sub> nanocrystals were coated as a thin film absorber layer for photovoltaic cells by doctor blading, yielding cell efficiency of 1.26%.

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## 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]. CuInS<sub>2</sub> (CIS) is a I-III-VI<sub>2</sub> 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)<sub>5</sub> 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

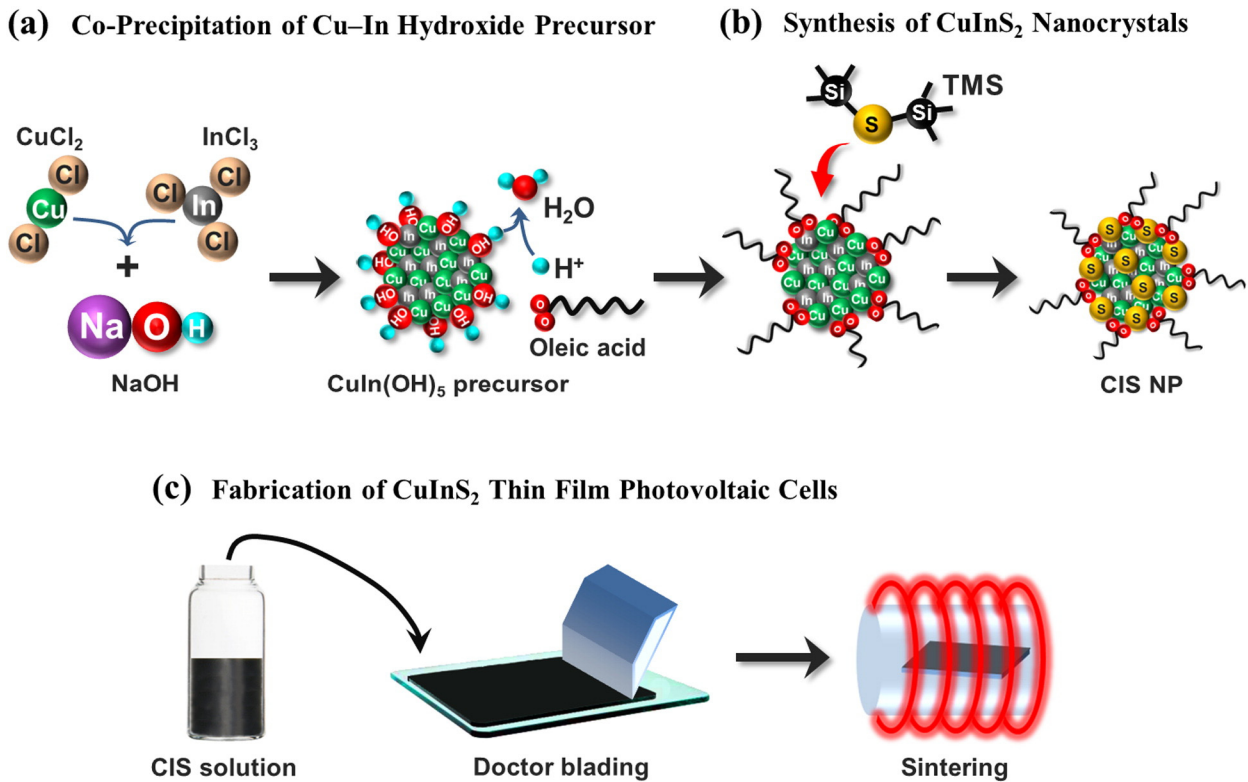
Copper(II) chloride, indium(III) chloride, sodium hydroxide, ammonium sulfide, oleic acid (OA), oleylamine (OLAM), 1-octadecene, bis(trimethylsilyl) sulfide, formamide, cadmium sulfate, thiourea, ammonium hydroxide, and chloroform were purchased from Sigma-Aldrich. Hexane, ethanol, 2-propanol, and acetone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

### 2.2. CuIn(OH)<sub>5</sub> precursor synthesis

To prepare the CuIn(OH)<sub>5</sub> precursor, 1.344 g of CuCl<sub>2</sub>, 2.211 g of InCl<sub>3</sub>, 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

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**Fig. 1.** (a) Co-precipitation of CuIn(OH)<sub>5</sub> precursor by using CuCl<sub>2</sub>, InCl<sub>3</sub>, and NaOH in aqueous solution; (b) preparation of CIS NCs by using bis(trimethylsilyl) sulfide; (c) thin film fabrication of CIS by using doctor blading coating.

with a mixture of ethanol and deionized water three times, yielding CuIn(OH)<sub>5</sub> precursor as powder.

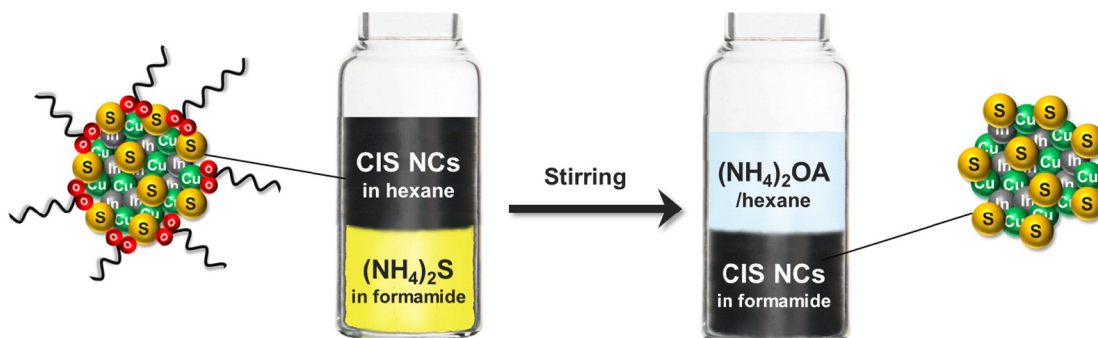
### 2.3. CuInS<sub>2</sub> nanocrystal synthesis

CuIn(OH)<sub>5</sub> 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-octadecene 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. CuInS<sub>2</sub> 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 H<sub>2</sub>S gas. CdS buffer layer was added by means of a chemical bath deposition method; the substrate was immersed in an aqueous solution of CdSO<sub>4</sub> (1.161 g, 50 mL), SC(NH<sub>2</sub>)<sub>2</sub> (2.88 g, 25 mL), and 28–30%



**Fig. 2.** Removal of OA ligands from as-synthesized CIS NCs and replacement to formamide.

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