

# Spray – casting $\text{CuInSe}_2$ nanoink onto Au and Mo coated substrates to fabricate photovoltaics

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**ABSTRACT:** Photovoltaic devices (PVs) were fabricated by spray-coating an ink of copper indium diselenide  $\text{CuInSe}_2$  (CIS) nanocrystals as the light-absorbing layer. Without high-temperature post-deposition annealing, PVs were made on glass substrates with power conversion efficiencies of up to 1.5% and 0.9%, for Au and Mo coated respectively, under AM 1.5 illumination. UV–Vis spectrophotometer in the wavelength range 350–1500 nm. X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) analysis it is evident that  $\text{CuInSe}_2$  have the chalcopyrite structure as the major phase and no secondary phase with a preferred orientation along (112) direction and The atomic ratio of Cu : In : Se in the nanocrystals is nearly 1 : 1 : 2.

**Keywords:**  $\text{CuInSe}_2$ ; nanoink; spray – casting; photovoltaic.

## 1. Introduction

$\text{CuInSe}_2$  (CIS) and  $\text{Cu(In,Ga)Se}_2$  (CIGS) are some of the most promising thin film PV materials. CIGS has a band gap in the appropriate range (1.0–1.7 eV depending on the Ga content), it is a strong light absorber, and has the highest recorded efficiency of all thin film PV materials of just over 20% [1-4].

Thin film PVs with lower manufacturing cost, like amorphous Si, copper indium gallium diselenide (CIGS) and CdTe, are gaining marketshare, but still require significant cost reductions to enable widespread adoption[2].

$\text{CuInSe}_2$  (CIS) and its alloys with gallium and sulfur are considered as an ideal photovoltaic absorber layer for thin film solar cells owing to their favorable electrical properties and long-term stability[5].

There is interest in enhancing performance using nanostructured materials as well as lowering manufacturing costs by using new materials that can be deposited without the need for high temperature and vacuum processing[6].

Here, we report the use of an ink of copper indium diselenide (CIS) nanocrystals that can be spray-coated under ambient conditions onto a Molybdenum (Mo) and Gold (Au) coated sodalime glass substrates to fabricate PVs was reported. There is an active search to identify semiconductor nanocrystals for photovoltaic devices (PVs) with low cost and high efficiency. Nanocrystals represent an alternative to organic PV materials, as they can be synthesized in industrial-scale quantities, dispersed and handled in solvents, and deposited easily on large-area substrates, with potentially better air- and photostability and higher performance. To date, the highest reported efficiency under AM 1.5 illumination from a nanocrystal-based PV without high temperature processing is just over 6% using PbS nanocrystals[7].

## 2. Experimental details

### Chemicals

Oleylamine (OLA;>70%), tributylphosphine (TBP; 97%), copper(I) chloride ( $\text{CuCl}$ ; 99.995+%), indium(III) chloride ( $\text{InCl}_3$ ; anhydrous 99.99%), elemental selenium (99.99%), cadmium sulfate ( $\text{CdSO}_4$ , 99.999%) from Aldrich Chemical Co.; ammonium hydroxide (18M  $\text{NH}_3$ , ACS certified), toluene (99.99%), ethanol (absolute), from Fisher Scientific; and thiourea (99.999%) from Fluka. Oleylamine was degassed by three cycles of freeze-

pump-thaw. All other chemicals were used as received without further purification. Copper (I) chloride, indium (III) chloride, TBP and degassed OLA were stored in a nitrogen-filled glovebox to prevent degradation.

### CIS nanocrystal synthesis

CIS nanocrystals were synthesized as previously described[2,6]. 5 mmol of CuCl (0.45 g) and 5 mmol of InCl<sub>3</sub> (1.11 g) was combined with 50 ml of degassed OLA, and a magnetic stir bar in a 100-mL three neck flask in a nitrogen-filled glovebox. The flask was sealed by a condenser-stop cock setup and two septa; the flask was removed from the glovebox and mounted on a Schlenk line. The reaction mixture was heated up to 110 °C, degassed for 10 minutes by pulling vacuum on the vessel and purged with clean nitrogen for 5 minutes. While maintaining the nitrogen environment, the reaction vessel was heated to 180 °C and 10 ml solution of 1 M Se in TBP (0.79 g Se powder and 10 ml TBP) was injected into the reaction vessel. The reaction mixture temperature was raised to 240 °C as quickly as possible and the reaction was allowed to proceed for 10 minutes. The heating mantle was removed and the reaction was cooled slowly to room temperature. After cooling, the reaction mixture was transferred to a glass centrifuge tube. 10 ml of ethanol was added to the centrifuge tube and the mixture was centrifuged at 4500 RPM for 10 minutes. The supernatant was discarded and the solid precipitate was dissolved in 10 ml of toluene. The new solution was centrifuged at 4500 RPM for 10 minutes to remove larger and poorly capped nanocrystals. The supernatant was transferred to a new glass centrifuge tube and the solid precipitate discarded. Ethanol was added drop-wise to the particle solution until a turbid mixture was achieved. The reaction was centrifuged again at 4500 RPM for 10 minutes. The supernatant was discarded and the precipitate dissolved in toluene to achieve a 20 mg/ml solution.

### Materials characterization

For morphological structure studies, transmission electron microscopy (TEM) was performed using a JEOL 2010F TEM at 200 kV accelerating voltage. TEM samples were prepared by drop casting from chloroform onto a 200 mesh nickel grid with a carbon film (Electron Microscopy Sciences). Energy dispersive X-ray spectroscopy (EDS) was carried out using an Oxford INCA EDS detector on the JEOL 2010F TEM. Scanning electron microscopy (SEM) was performed on a Zeiss Supra 40 VP SEM operated at 5 keV accelerating voltage through an In-

lens detector with samples grounded using copper tape.

For structural study X-ray diffraction (XRD) was performed using a Rigaku R-Axis Spider diffractometer with an image-plate detector and Cu K $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation operated at 40 kV and 40 mA. XRD samples were prepared by drying a drop of concentrated nanoparticle dispersion onto a glass slide in a glovebox. The nanocrystal powder was then suspended on a 0.5 mm nylon loop using mineral oil for analysis. Samples were scanned for 15 min while rotating at 2°/s. The 2D diffraction patterns were integrated using the Rigaku 2DP powder processing suite with subtraction of the background scattering from the nylon loop and mineral oil.

UV-vis-NIR absorbance spectroscopy was performed at room temperature using a Varian Cary 500 UV-vis-NIR spectrophotometer in order to study the optical properties. Nanocrystals were dispersed in toluene in quartz cuvettes. Absorbance was also measured for thin, optically transparent nanocrystal films deposited by spray-coating on a quartz substrate.

### PV device fabrication

Conductive back contacts (Mo, Au) were deposited separately on sodalime glass (Delta Technologies, 25 mm x 25 mm x 1.1 mm) after cleaned by sonication in an acetone/isopropanol mixture, followed by rinse with (DI) water, and drying under a nitrogen. Molybdenum of 500 nm thick (99.999% Lesker) was deposited by RF sputtered while the gold was thermally evaporated. 10 mg mL<sup>-1</sup> solutions of nanoparticles were prepared for the spray-deposition. CIS nanocrystal layers were spray-coated with an airbrush (SONOTEK) operated at 1.6 psig of head pressure. A CdS buffer layer was deposited by chemical bath deposition following procedures described by McCandless and Shafarman[8]. Briefly, A CdS buffer layer was deposited by dropping 0.7 mL of a CdS precursor solution (1.25 mL of 15 mM CdSO<sub>4</sub>, 2.2 mL of 1.5 M thiourea, and 2.8 mL of 18 M NH<sub>4</sub>OH in water) onto the CIS nanocrystal film heated to 95 °C on a hot plate and covered with an inverted crystallization dish for 2 min. The substrate was removed from the hot plate, rinsed with DI water, and dried with a stream of compressed air. Top layers of ZnO and ITO were deposited by RF sputtering from a 40 nm ZnO target (Lesker, 99.9%) in a 0.5% O<sub>2</sub> in Ar atmosphere (Praxair, 99.95%) and a 300 nm of ITO target (Lesker, 99.99% In<sub>2</sub>O<sub>3</sub>:SnO<sub>2</sub> 90:10) in Ar atmosphere (Praxair, research grade). ZnO and ITO are deposited selectively onto 8

rectangular regions with active device areas of  $0.08 \text{ cm}^2$  ( $8 \text{ mm}^2$  a  $4 \text{ mm} \times 2 \text{ mm}$  rectangle). Silver paint was applied for electrical contact to the devices.

### PV device testing

PV device response was measured using a Keithley 2400 General Purpose Sourcemeter under solar simulation using a Newport Xenon Lamp Solar Simulator with an AM1.5 filter ( $100 \text{ mW/cm}^2$ ). Intensity of the light source was calibrated using a NIST calibrated Si photodiode (Hamamatsu, S1787-08). Different fractions of solar spectrum were generated by placing colored glass cutoff filters (Newport) directly in the path of light beam emanating from the solar simulator. Incident photon conversion efficiency (IPCE) was measured using a home-built device with lock-in amplifier (Stanford Research Systems, model SR830) and monochromator (Newport Cornerstone 260 1/4M). IPCE was calibrated with Si and Ge photodiodes (Hamamatsu).

## 3. Results and discussion

### CuInSe<sub>2</sub> nanocrystal inks

Figure 1 shows TEM, SEM, and XRD data for the oleylamine capped CIS nanocrystals. The nanocrystals are composed of chalcopyrite CIS with an average diameter of 12 nm and a slightly irregular, faceted shape. The atomic ratio of Cu : In : Se in the nanocrystals determined by EDS is nearly 1 : 1 : 2. The nanocrystals disperse in various organic solvents, including chloroform, hexane, toluene and acetone. Toluene was used as the dispersing solvent for the nanocrystal inks used to fabricate devices, as it provided the most uniform coatings of the solvents that were tested. An SEM image of a spray-deposited 200 nm thick nanocrystal film is shown in Figure 2c. The film has uniform thickness and is nearly free of drying cracks, which is crucial for obtaining functional PVs without electrical shorts. Film uniformity is still one aspect of the device fabrication process that requires further optimization.

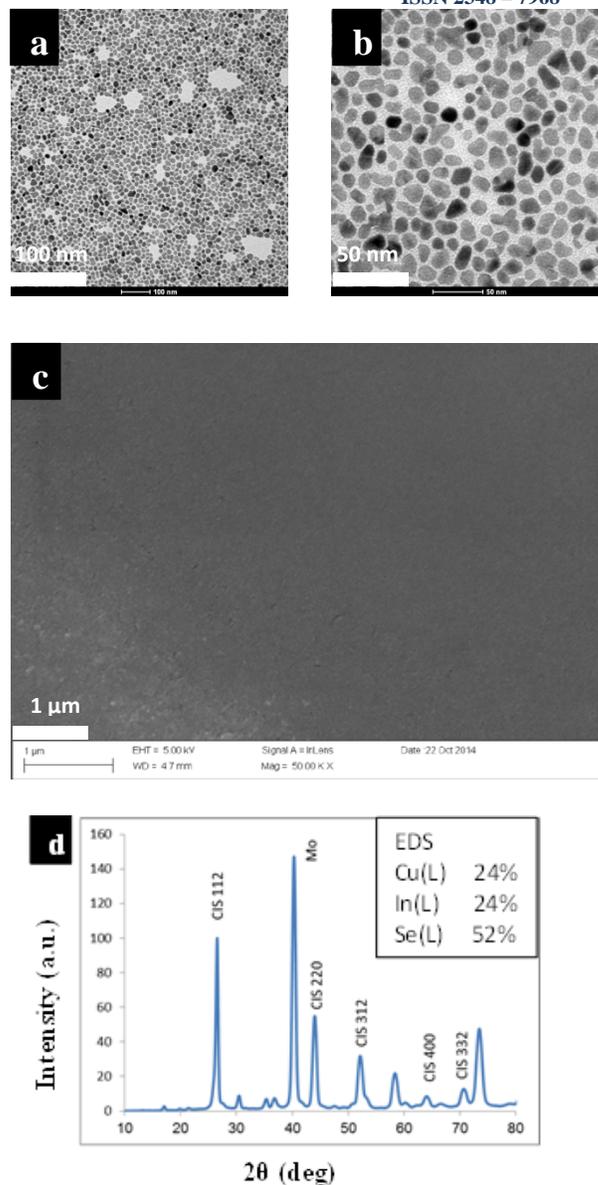


Fig. 1 (a, b) TEM images of CIS nanocrystals; (c) an SEM image of a film of CIS nanocrystals spray-deposited from a toluene dispersion; (d) XRD pattern of CIS nanocrystals indexed to chalcopyrite CIS (PDF#97-006-8928). The inset in (d) is the average Cu, In, and Se composition determined by EDS of a field of nanocrystals

## 4. PV device fabrication

PV devices were fabricated by spray-casting of the CuInSe<sub>2</sub> nanocrystal ink onto Au and Mo back contacts on glass substrates. Nanocrystal films with uniform CIS nanocrystal layer are shown in Fig. 2. Dark and light I-V curves for the device with highest power conversion efficiency (PCE), (a) Au coated substrate

and (b) Mo as a back contact.(c) a cross-sectioned PV device with a layer of CIS thickness with few pinholes or cracks are obtained using this method. Devices have been made using this approach with power conversion efficiencies under AM1.5 illumination of up to 1.5% for Au and 0.966% for Mo.

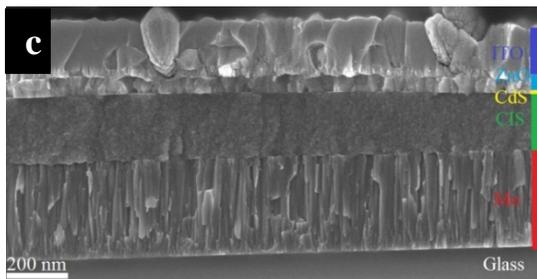
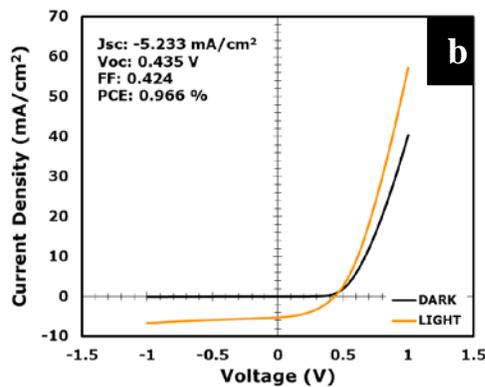
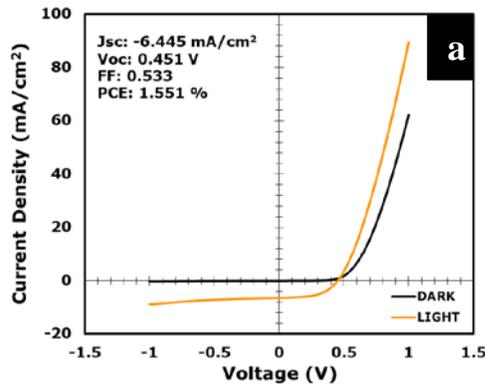


Figure 2 shows the dark and light I-V curves for the device with highest power conversion efficiency (PCE), and cross-sectional SEM image of a PV device made by spray-casting of CIS nanocrystal layer.

The device has a similar architecture as those with the highest reported efficiency for CIGS, consisting of layers of glass/Mo or Au/CIS(nc)/CdS/ZnO/ITO. No high-temperature annealing or selenization of this

device was carried out. This particular device had a power conversion efficiency under AM 1.5 simulated sunlight of 1.5%. Since the absorber layers are not processed at high temperature, alternative substrates and contacts can be used, including transparent conductive ITO or mechanically flexible plastic. Figure 3 shows photographs of PV device that could be prepared by spray-casting CIS nanocrystal absorber layers.

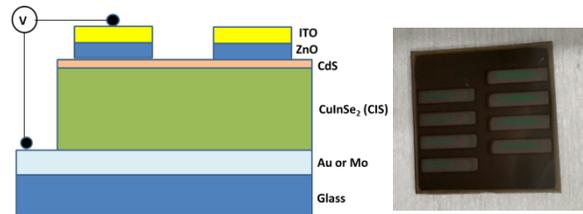


Fig. 3 (Right) Photographs of PVs fabricated by spray-casting CIS nanocrystals on Mo substrate. (left) Illustration of the device layer structure as viewed from the side.

The devices generally consist of a sandwiched construction of the p-type light-absorbing nanocrystal layer interfaced with an n-type semiconductor (CdS, ZnO) positioned between two planar conducting contacts. The thin CdS layer (5–10 nm) also helps protect the CIS nanocrystal layer during sputtering of the window layer. Au has a higher work function than Mo and should make a better back contact metal for the p-type CIS nanocrystals layer. Au is not used in conventional CIGS PVs because it cannot withstand the high-temperature annealing conditions. We have found that CIS nanocrystal PVs made with Au contacts on glass outperform those made with Mo contacts. Au contacts are also easy to deposit on plastic substrates for flexible devices.[2]

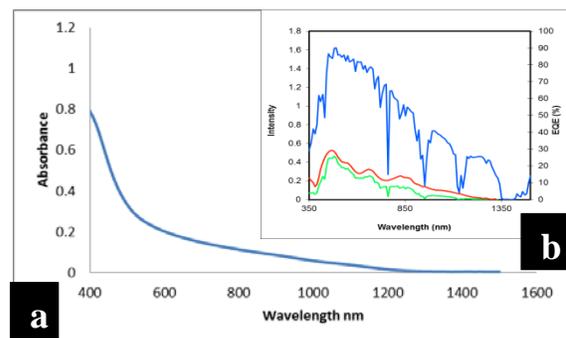


Fig. 4 (a) UV–vis–NIR absorbance spectra of a 100-150 nm thick CIS nanoparticles film (b) External quantum efficiency (EQE) of a PV device made with a spray-casting CIS nanocrystal layer.

Figure 4 shows UV–vis–NIR absorbance spectra and External quantum efficiency (EQE) of a PV device made with a spray-casting CIS nanocrystal layer. EQE is determined from the incident photon conversion efficiency (IPCE) spectra, which is a measure of short circuit current as a function of light wavelength. Figure 4b shows the external quantum efficiencies of a CIS nanocrystal device as a function of photon wavelength. The external quantum efficiency (EQE) also known as incident photon conversion efficiency (IPCE) spectra are determined by measuring the short circuit current (at zero bias) when the device is illuminated with varying photon wavelength. The EQE are not equivalent to power conversion efficiencies, but nonetheless provide revealing data about internal losses due to electron-hole recombination. The EQE is lowest near the CIS optical gap due to low light absorption, but extends across all visible wavelengths, indicating that the devices are functioning via light absorption by the nanocrystals.

## 5.conclusion

PV devices with reproducible and reliable power output were fabricated by spray-casting. CIS nanocrystals without postdeposition annealing. Layered Au/CIS/CdS/ZnO/ITO and Mo/CIS/CdS/ZnO/ITO PV devices exhibited power conversion efficiencies of up to 1.5% and 0.9% respectively under AM 1.5 illumination. The device efficiency still requires significant improvement. A nanocrystals ink that could be used to fabricate high efficiency PVs without needing for high-temperature processing.

## 6.Acknowledgment

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