

# Preparation of Copper Iodide (CuI) Thin Film by In-Situ Spraying and Its Properties

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**Abstract.** Perovskite based solar cells have attracted interest as low-cost and high-efficiency solar cells due to their great performance, with efficiency up to 20.1%. One type of hole transport material (HTM) used in perovskite based solar cells is copper iodide (CuI) thin film. CuI is inexpensive and has high mobility compared to other HTMs commonly used in perovskite based solar cells. However, diisopropylsulfide solvent, which is used to dissolve CuI in the preparation process, is a malodorous and toxic compound. Therefore, the objective of this research was to develop a synthesis method for CuI thin film with in-situ spraying, a low-cost, safe and easy fabrication method. As precursor solution,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was dissolved in ammonia and KI aqueous solution. The precursor solution was then sprayed directly onto a glass substrate with appropriate temperature to form CuI film. The prepared thin films were characterized by X-ray diffractometer, UV-Vis spectrophotometer, scanning electron microscope and four-point probes to study their properties.

## 1. Introduction

Recently, a perovskite based solar cell has achieved 20.1% efficiency, which is higher than the efficiency of other third-generation solar cells, such as dye sensitizer solar cells (DSSC) and organic solar cells [1]. In general, perovskite solar cells consist of absorber, electron transport material (ETM), hole transport material (HTM), transparent conducting material, and electrode layers. The absorber layer, which consists of perovskite, plays a role in harvesting sunlight and generating electron-hole pairs. Common perovskite materials used as absorber are organic-inorganic halide perovskites such as  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ .

The hole transport material (HTM) serves as hole conductor from the perovskite material to the electrode. Organic/polymer materials are widely used as hole transport material in perovskite solar cells, for example Spiro-OMeTAD and P3HT. Perovskite solar cells with Spiro-OMeTAD as HTM layer have shown the highest efficiency so far [2]. Spiro-OMeTAD is an organic p-type semiconductor that is relatively expensive, even more expensive than the perovskite material. It is a challenge to



replace the HTM with a new HTM with high mobility that is inexpensive and easy to fabricate. Inorganic p type semiconductors, such as copper iodide (CuI), are among the candidates for functioning as HTM [3].

J.A. Christians et al. (2014) have reported on the use of CuI as HTM in perovskite based solar cells, which reached 6% efficiency. Surprisingly, perovskite solar cells with CuI as HTM have shown a stable performance until 54 days of storage in ambient conditions [3]. However, diisopropylsulfide solvent, which is a malodorous and toxic compound, was used in order to dissolve the CuI prior to the filming process. CuI has also been used in DSSC as a solid state electrolyte (like HTM). The CuI film was successfully prepared by dissolving CuI powder in acetonitrile solvent prior to the spin coating process [4]. However, since acetonitrile solvent could dissolve the perovskite layer, it is not appropriate for use in perovskite based solar cells [5]. To solve this problem, a new facile method for preparing CuI film is required. In this report, CuI thin film was prepared with a newly developed method involving in-situ spraying deposition. To the best of our knowledge, there are no reports about the preparation of CuI thin film for application in perovskite based solar cells, using in-situ spraying techniques.

## 2. Experimental Procedure

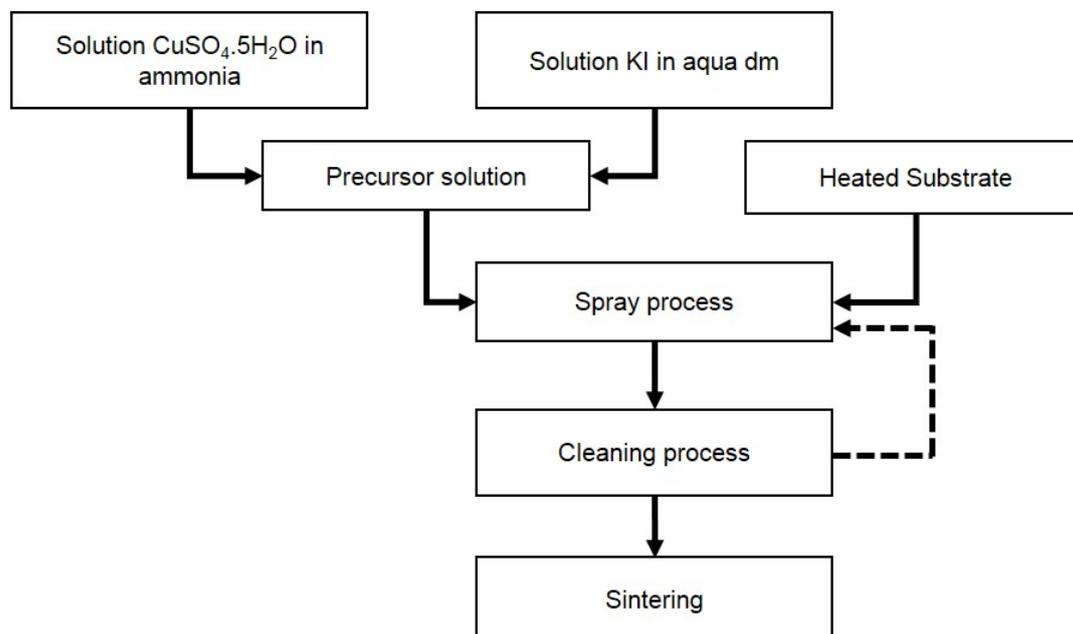
### 2.1. Material preparation

CuI thin film was synthesized by in situ spraying. Deposition of CuI was carried out at ambient atmosphere inside a fume hood. In our experiment, we used 1 x 1 cm glass substrates that were cleaned by NaOH 10 %wt, aqua dm, acetone and 2-propanol, respectively, using an ultrasonic bath. Precursor solution was prepared by mixing the  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution in ammonia and the KI solution in demineralized water with molarity ratio 1:2. The molarity of the precursor solution was varied as follows:

**Table 1.** Composition of precursor solution

Molarity (M)	Mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (mg)	Mass of KI (mg)	Volume of ammonia (ml)	Volume of aqua dm (ml)
0.05	0.062	0.083	5	5
0.10	0.125	0.166	5	5
0.15	0.187	0.249	5	5
0.20	0.250	0.332	5	5

**Figure 1** shows the experimental procedure to synthesize CuI thin film. The precursor solution was sprayed onto a substrate that was heated on a hot plate at 100 °C. The CuI was sprayed in several cycles. In each cycle, 0.5 ml precursor was sprayed onto the substrate. After 1 minute, the film was cleaned by 5 ml demineralized water. The cleaning process removes  $\text{K}_2\text{SO}_4$  from the film. The number of cycles depends on the total precursor volume that is to be sprayed onto the substrate. In this experiment, we used 3 ml precursor for 1 substrate. After the spray cycles were finished, the CuI thin film was sintered for 15 minutes at 100 °C. Furthermore, we also varied the sintering temperature at 80 °C, 100 °C, 120 °C and 150 °C.



**Figure 1.** Experiment procedure chart of CuI thin film.

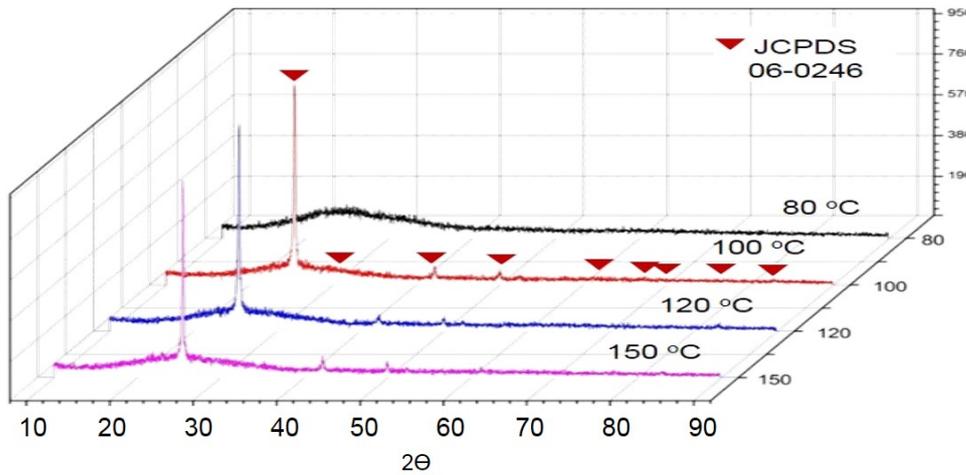
## 2.2. Characterization

All samples were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Vis spectrophotometry and four-point probes. An X-ray diffractometer (Philips Analytical PW 1710 BASED) was used in this measurement, with a step size of  $0.02^\circ$  for Cu  $K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). SEM measurements were carried out on a field emission scanning electron microscope (Jeol JCM-6000 Bench-top SEM, Japan). Finally, a UV-Vis spectrophotometer (Ocean Optik HR2000CG-UV-NIR) and four-point probes (homemade) were used to identify the chemical bonding and resistivity, respectively.

## 3. Result and discussion

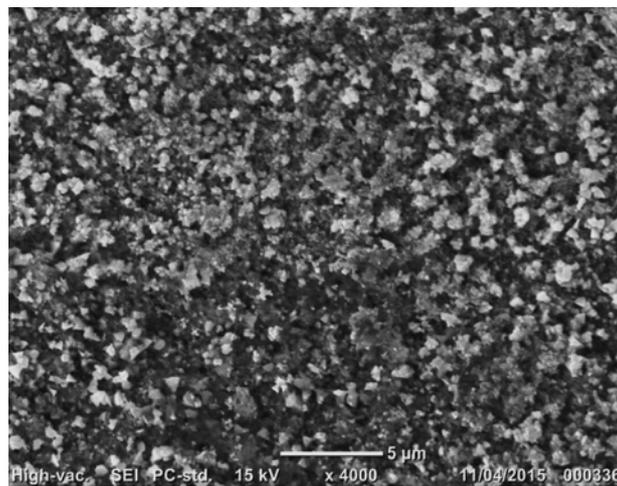
To investigate crystal structure, the CuI thin film samples prepared with 0.05 M concentration, 1.5 ml volume precursor, 15 minutes sintering time and variation of sintering temperatures were characterized using XRD. **Figure 2** shows the XRD result for the CuI thin film with variations of sintering temperature. From this result, it can be seen that the CuI thin film with  $80^\circ\text{C}$  sintering temperature had no diffraction peaks. This indicates that the CuI thin film was still in amorphous form. Starting from  $100^\circ\text{C}$ , the crystallinity of the CuI thin film can be seen from several diffraction peaks. The XRD patterns of the CuI thin film corresponded well to zinc blende face centered cubic CuI (JCPDS, 06-0246).

The crystallite size of the CuI thin film was calculated from the XRD result by using Scherrer's formula [6]. Based on the calculated crystallite size of the CuI thin films, the crystallite size increased with increasing sintering temperature. A higher temperature makes it easier for the particles to fuse and bind to each other. As a consequence, the crystal quality also improves.



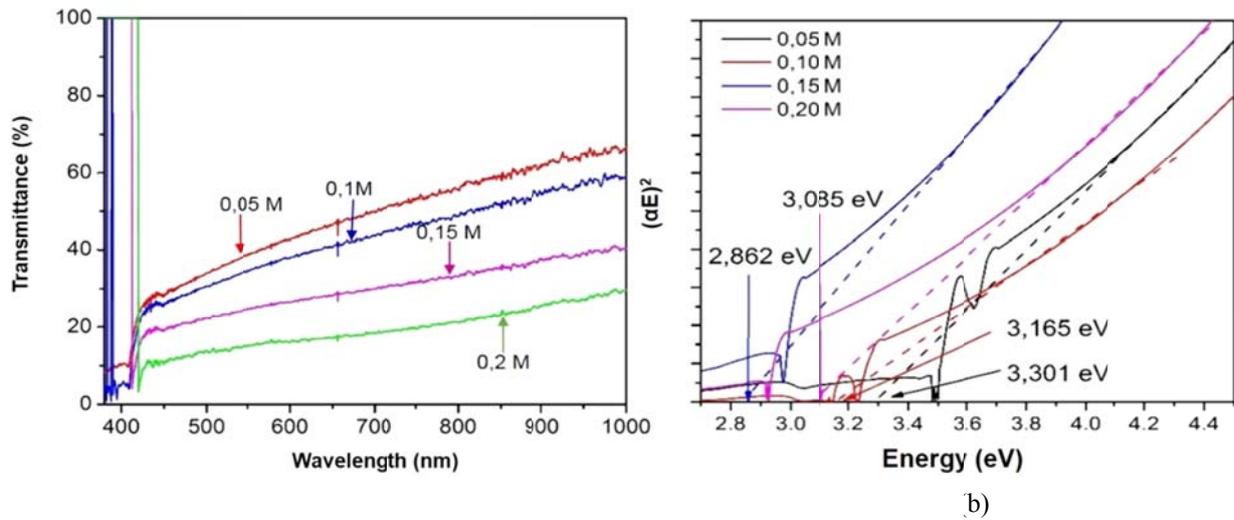
**Figure 2.** XRD result and crystallite size for the CuI thin film with variations of temperature.

**Figure 3** shows an SEM image of the CuI thin film with sintering temperature at 100 °C and molarity of the precursor at 0.05 M. Based on this image, the CuI thin film exhibited a smooth layer without agglomeration of CuI particles. Moreover **Figure 3** shows irregular small holes, which originated from  $K_2SO_4$  due to leaching.



**Figure 3.** SEM image of CuI thin film.

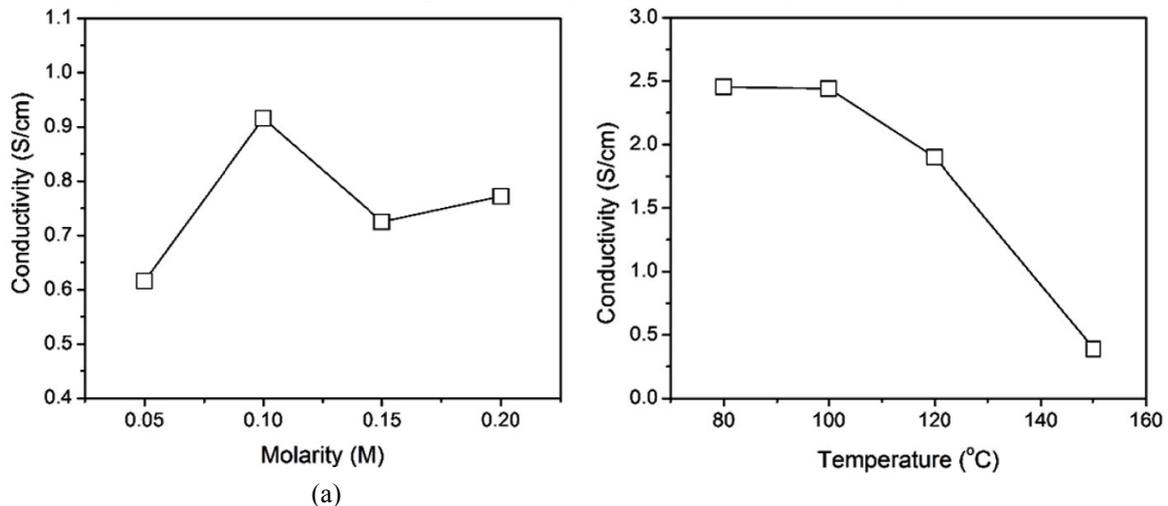
**Figure 4(a)** shows the transmittance spectra of the CuI thin film with different molarities of the precursor. From this result, it can be seen that all CuI thin films exhibited very low transmittance. The increasing precursor molarity decreased the transmittance of the CuI thin films. This indicates that molarity affects the optical properties of CuI thin film. A higher precursor molarity may provide more CuI particles that can increase scattered or absorbed light.



**Figure 4.** (a) Transmittance spectra of CuI thin film, and (b) Tauc plot band gap energy of CuI thin film.

Furthermore, the band gap energy was determined from the transmittance spectra using Swanepoel’s method and the Tauc Plot. In this experiment, we used free software from PARAV to determine the band gap of the CuI thin film [7]. **Figure 4(b)** shows the Tauc plot of the CuI thin film with variation of precursor molarity. The calculated band gap energy shows values of 3.301 eV for 0.05 M, 3.165 eV for 0.10 M, 2.862 eV for 0.15 M and 3.085 for 0.20 M, respectively. The small variation of the band gap energy may be caused by a defect in the film [8].

The electrical properties of the CuI thin films with variation of molarity of the precursor were measured by four-point probe. **Figure 5(a)** shows the effect of molarity on the conductivity of the CuI thin films. It shows that precursor with molarity 0.1 M gave optimum conductivity. This originates from the presence of Cu and I ions that provide free electrons. Moreover, the derivation of conductivity for CuI thin film with higher molarity may be caused by inhomogeneous film.



**Figure 5.** (a) Conductivity of CuI thin film with variation of precursor molarity, and (b) conductivity of CuI thin film with variation of temperature.

**Figure 5(b)** shows the dependence of conductivity on sintering temperature. The increment of the sintering temperature decreased the conductivity of the CuI thin film. This is due to the stoichiometric excess of iodine in CuI. In small amounts, excess iodine creates holes acting as electron acceptors and increases conductivity [9, 10]. Meanwhile, an increment of the temperature can remove iodine and hence the conductivity of the CuI thin film decreases.

#### 4. Conclusion

CuI thin film with in-situ spraying, a low-cost, safe and easy fabrication method was successfully synthesized. The synthesized processed was done by dissolving  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in ammonia and KI aqueous solution. The precursor solution was then sprayed directly onto a glass substrate with appropriate temperature to form CuI film. The XRD patterns of the CuI thin film corresponded well to zinc blende face centered cubic CuI. The SEM image shows that the CuI thin film exhibited a smooth layer without agglomeration of CuI particles. The prepared samples have calculated band gap energy around 3.0 eV. It gives higher conductivity for precursor with molarity 0.1 M which originates from the presence of Cu and I ions that provide free electrons.

#### Acknowledgements

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#### References

- [1] [http://www.nrel.gov/ncpv/images/efficiency\\_chart.jpg](http://www.nrel.gov/ncpv/images/efficiency_chart.jpg).
- [2] Zhou, H., et al. 2014 Photovoltaics. Interface engineering of highly efficient perovskite solar cells. *Science* **345**(6196) 542-6.
- [3] Christians, J.A., R.C. Fung, and P.V. Kamat 2014 An inorganic hole conductor for organo-lead halide perovskite solar cells. Improved hole conductivity with copper iodide *J Am Chem Soc* **136**(2) 758-64.
- [4] Perera, V.P.S. and K. Tennakone 2003 Recombination processes in dye-sensitized solid-state solar cells with CuI as the hole collector *Solar Energy Materials and Solar Cells* **79**(2) 249-255.
- [5] Niu, G., X. Guo, and L. Wang 2015 Review of recent progress in chemical stability of perovskite solar cells *J. Mater. Chem. A* **3**(17) 8970-8980.
- [6] Amalina, M.N. and M. Rusop 2013 Investigation on the I<sub>2</sub>:CuI thin films and its stability over time *Microelectronic Engineering* **108** 106-111.
- [7] Ganjoo, A. and R. Golovchak 2008 Computer program PARAV for calculating optical constants of thin films and bulk materials: Case study of amorphous semiconductors *J. Optoelectronics and Adv. Mat.* **10** 1328-1332.
- [8] Rusop, M.N.A.a. 2011 Effect of the precursor solution concentration of Copper (I) Iodide (CuI) thin film deposited by mister atomizer method *IEEE Symposium on Industrial Electronics and Applications (ISIEA)* 440-444.
- [9] K. Tennakone, G.R.R.A.K., I.R.M. Kottegoda, V.P.S. Perera, G.M.L.P. Aponsu, K.G.U. Wijayantha 1998 Deposition of thin conducting films of CuI on glass *Solar Energy Materials and Solar Cells* **55** 283-289.
- [10] Amalina, M.N., et al. 2013 The Properties of Copper (I) Iodide (CuI) Thin Films Prepared by Mister Atomizer at Different Doping Concentration *Procedia Engineering* **56** 731-736.