

Structural and Morphological investigation of Copper (I) Iodide utilized as a Hole Transport Layer in Perovskite Solar Cells

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Hybrid Halide Perovskite (HHP) solar cells are considered as a most promising candidate for the next generation of photovoltaics. The charge transport layer namely, the hole transport layer (HTL) plays a vital role in the device performance of perovskite solar cells (PSCs). Besides the power conversion efficiency (PCE), the stability and cost are two significant factors for deciding the commercialization of PSC device. The HTL bears a significant portion of the PSC's cost, and the degradation of the PSCs occurs in the presence of organic HTL. The inorganic HTL, Copper (I) iodide (CuI), a p-type semiconductor, is a good choice for HTL due to its chemical stability, low cost, and low band gap. In this work, we deal with the structural and morphological investigation of CuI thin film using X-ray Diffraction and Scanning Electron Microscopy analysis, respectively. The utilization of such inorganic HTL will help the researchers in fabricating the low-cost PSC devices.

1 Introduction

In recent years, the demand for energy has increased globally but the number of non-renewable sources for generating energy are limited, so there is a need to look for the renewable energy sources nowadays. It is crystal clear to all of us how important is the harvesting of renewable energy. Among all the renewable sources, the harvesting of solar energy is worthy as the sun is the richest and cost free source of energy. Harvesting of solar energy by perovskite solar cells (PSCs) is among the best topics for the researchers across the globe. From 2009 to 2023, the reported power conversion efficiency (PCE) reached from 3.8%¹ to 26.1 %². Past decade witnessed the successful candidature of hybrid halide perovskite (HHP) in high-performance photovoltaic sector. The layers of HHP solar cells are starting from FTO/ITO coated glass, electron transport layer (ETL), absorber layer, hole transport layer (HTL) and metal contacts³. The HTL in PSCs plays a vital role in device performance and also in the determination of the overall flexibility and cost of resultant solar cells⁴. So, developing an efficient bifunctional and cost-effective HTL is very important for developing the efficient and stable PSCs.

The HTL is a key part of HHP based solar cells and there are many efficient materials for HTL like Spiro-OMeTAD, CuI, Cu₂O, NiO_x, PEDOT:PSS, PTAA. Since in PSCs, the efficiency, cost effectiveness and stability performance are the main concerns to be resolved. Therefore, using CuSCN as HTL is a good move as it provides a good chemical stability and can be long lasting at the high temperature that is generally needed in the fabrication process of PSCs cells. While the other organic HTLs, for *e.g.* Spiro-OMeTAD, are very costly.

CuI is an earth-abundant material which makes it relatively inexpensive to produce and cost effective in comparison to other HTLs. It has high hole mobility, large band gap and better chemical stability. In 2014, Christians *et al.*⁵ first used CuI in PSCs and determined the efficiency of PSC device as 6 %. In 2017, Li *et al.*⁶ prepared the layer of CuI by facile spray-deposition method, which shows the PCE up to 17.6 %, having good stability and depressed hysteresis. Overall, the research work of studying the CuI as an efficient HTLs has the potential to make significant contributions to the fields of energy and electronics, as well as to our understanding of fundamental charge transport processes. Also, by studying the CuI as a HTL, we can draw new strategies to improve the efficiency and

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lifetime of the PSC devices. Keeping the importance of CuI as HTL in mind, we plan to investigate structural and morphological analysis of CuI thin films.

2 Materials and Method

Powder of Copper (I) iodide (CuI) and Ammonia solution have been used for the preparation of thin film of CuI. The precursor solution of CuI of 0.5 M was prepared by weighing 38.090 mg of CuI powder and mixed it with 4 mL of ammonia solution. The solution was then placed on a magnetic stirrer for 2 hours at room temperature. The glass substrates were cleaned with soap solution, acetone, de-ionized water and ethanol in ultra-sonicator for 10 minutes each. The substrates were then placed in the oven for 10 minutes to dry. After that substrates were placed on a hot plate and with the method of drop casting, a precursor solution was deposited on the substrate and finally the film was annealed at 110 °C. The crystal structure of CuI film was investigated in the range of 20-70° using X-ray Diffractometer (XRD) with Cu Kα-rays (λ = 1.54 Å). The scanning electron microscope (SEM) associated with energy dispersive X-ray spectroscopy (EDX) was used to investigate the morphology and elemental distribution of prepared sample.

3 Results and Discussions

The XRD pattern of synthesized CuI thin film is depicted in Fig. 1. The intense diffraction peaks at 2θ values of 25.89°, 42.64°, and 50.36° correspond to (111), (220), (311) planes of cubic CuI phase, respectively, which is consistent with previous work⁷.

The crystallite size was calculated using both Debye Scherrer formula and Williamsons-Hall (W-H) method. In W-H method, the crystallite size and strain are calculated from intercept and slope of βcosθ versus 4sinθ plot respectively as shown in Fig. 2, where β is full width at half maxima (FWHM), θ is Bragg angle. The crystallite size comes out to be 24.76 nm and

22.5 nm by W-H method and Debye Scherrer formula, respectively, which matches fairly with each other. The strain in CuI crystallites was also calculated from the slope in the W-H plot and found to be 4.26×10^{-4} .

The microscopic analysis of the synthesized sample is shown in Fig. 3. The plan-view SEM image *i.e.*, Fig. 3(a) displays the agglomeration of particles with

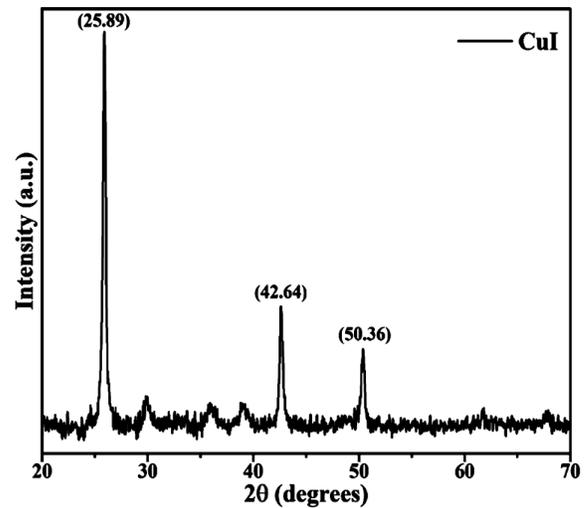


Fig. 1 — XRD plot for CuI thin film.

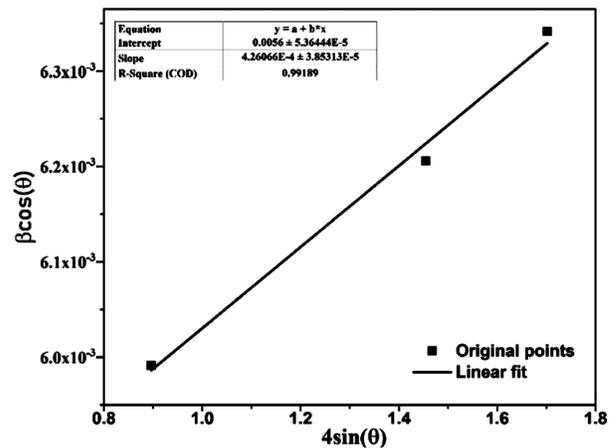


Fig. 2 — Williamsons Hall analysis plot of CuI.

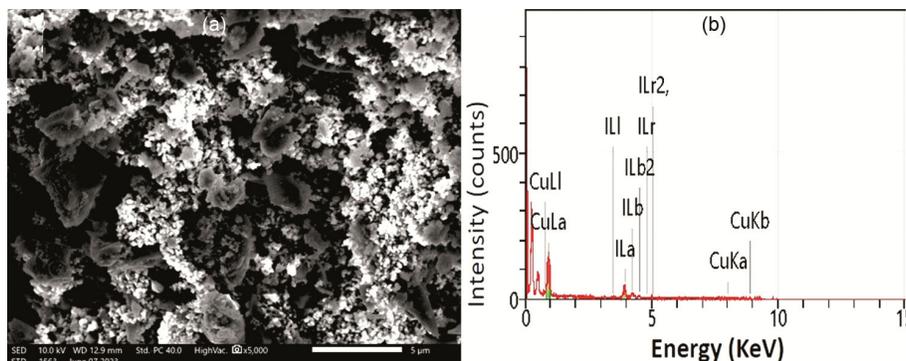


Fig. 3 — SEM with EDX image of CuI.

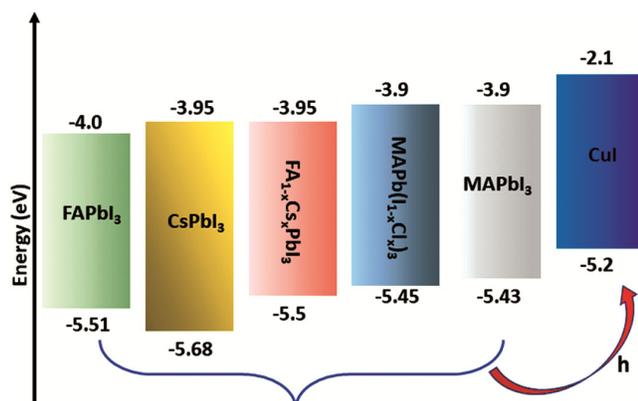


Fig. 4 — Energy band diagram for CuI and various absorber layers.

island like morphology. It was observed that the size of the particles got varied indifferently ranging from 200 nm to 8 μm . Further, to ascertain the stoichiometry of the sample, the EDX measurement was also performed as shown in Fig. 3(b). The EDX analysis confirmed the synthesis of CuI sample with a 42 % & 58 % concentration of copper and iodine, respectively. However, no traces of any other element or impurity were observed.

Further, in order to check the compatibility of CuI as HTL in PSCs, we considered various prominent organic/inorganic absorber layers such as MAPbI₃, FAPbI₃, CsPbI₃, Cs_xFA_{1-x}PbI₃, MAPb(I_{1-x}Cl_x)₃. The energy band diagram for different absorbers in PSCs and CuI is shown in Fig. 4.

The values of highest occupied molecular orbital (HOMO) level and lowest unoccupied molecular orbital (LUMO) level in energy band diagram are extracted from existing literature studies⁸⁻¹². It is found that there is a good band alignment between valance band of CuI and highest occupied molecular orbital (HOMO) of various organic/inorganic absorber layers. This alignment facilitates the efficient hole transport to the CuI from the absorber layer. In the nutshell, we can infer that CuI can be considered

as a suitable HTL for all studied organic/inorganic absorber layer in PSCs.

4 Conclusion

The sample of CuI was prepared by drop-casting method. The crystallize size was calculated using both Williamsons-Hall method and Debye Scherrer formula, which matches fairly with each other. Moreover, the strain in CuI was found to be 4.26×10^{-4} , which is very small. The scanning electron microscopy (SEM) image display agglomeration of particles with island like morphology. The EDX analysis confirmed the synthesis of CuI sample with a 42 % and 58 % concentration of Copper and Iodine, respectively. And no traces of impurity were observed. The energy band diagram of CuI with various absorber layers reflects the better compatibility of CuI as HTL in PSCs with the various studied organic/inorganic absorber layer.

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