

Effect of Copper Phthalocyanine Interfacial Layer on the Performance of Mixed Halide Perovskite Solar Cells

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Abstract. Organo metallic halide perovskite solar cells (PSCs) have attracted much attention due to the enhanced photovoltaic performance and wide absorption in the visible region. In this work, a perovskite solar cell device with mixed halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ as the active layer was fabricated in the normal device architecture and investigated. The effect of device performance was compared by introducing copper phthalocyanine (CuPc) as a hole transport layer (HTL). It is seen that device with a transport layer exhibits a better performance and power conversion efficiency (PCE) than the device without an HTL. The carrier mobility was determined using the space charge limited current (SCLC) method and found to be $0.0013\text{cm}^2/\text{Vs}$.

Introduction

Perovskite solar cells (PSCs) have got considerable attention since 2009 when the first cell was reported with a conversion efficiency of 3.8% [1]. Following the pioneer work of Miyasaka et.al in organic-inorganic methyl ammonium lead halide perovskites, ease of preparation and solution processability makes it interesting for photovoltaic applications [2]. The real success happened in 2012 when the efficiency had reached up to 10% [3][4] and at present, the reported efficiency is about 21.6% [5]. Though the commercialisation demands high efficiency, long term stability and behaviour of suppressed hysteresis [6].

PSCs make use of hybrid halide perovskite materials as the light absorbers and they possess crystal structure in the form ABX_3 where A and B are the cations. The cations A exist at the corners of the cubical structure and B in the middle of the octahedral sites set up by the X anions which exist in the middle of each face. The X consists of a halide and it can be fluorine, chlorine, bromine, iodine or a mixture of different halide atoms. Lead is the usually used small cation B. Tin can also be used, but it makes the structure less stable [7]. These small cations B together with the anions X form the inorganic part of the perovskite material. Methyl ammonium, ethyl ammonium or formamidinium constitute the organic part. The most investigated perovskite materials for photovoltaic applications are $\text{CH}_3\text{NH}_3\text{PbI}_3$ or the mixed halide $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ [8] due to their properties like intense wide band absorption, direct band gap, high carrier mobility and simple fabrication method [9]. The structures of the methyl ammonium halide [10] and copper phthalocyanine [11] are shown in Fig. 1.

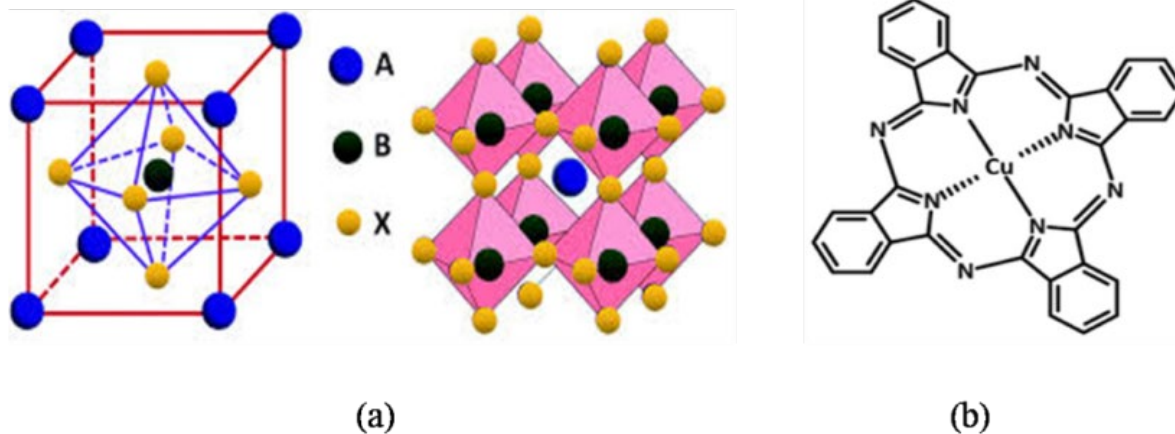


Fig. 1 Structures a) Organic-inorganic Methyl Ammonium Halide b) CuPc

Perovskite solar cell structures are generally classified into i) Inverted p-i-n and ii) Normal n-i-p structures [12] which are shown in Fig. 2.

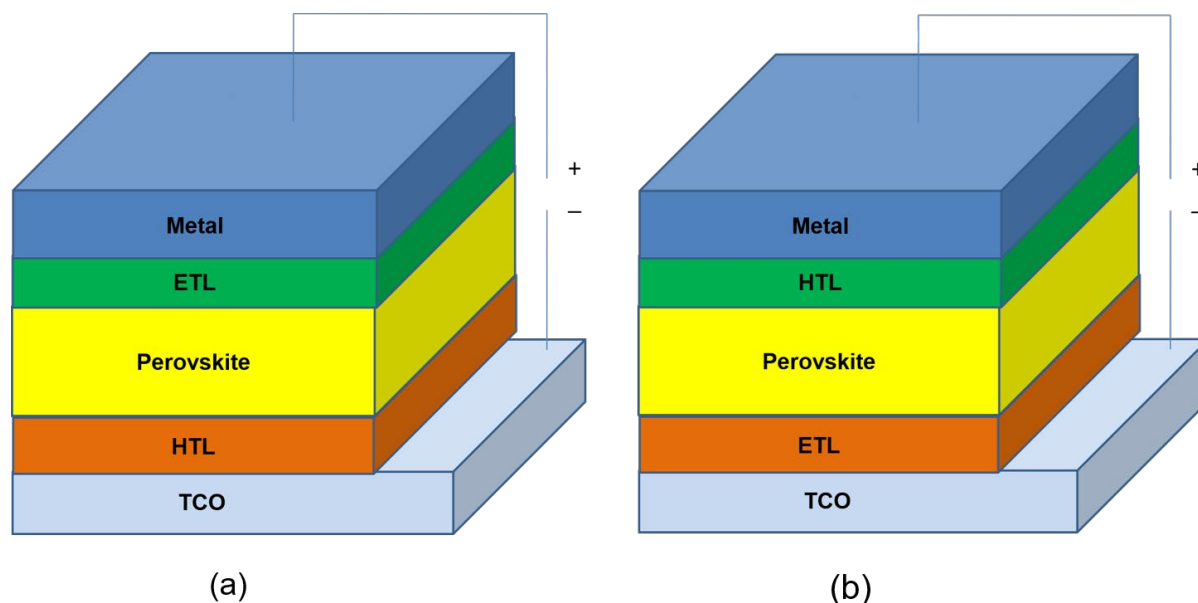


Fig. 2 (a) Inverse p-i-n and (b) Normal n-i-p

Device architecture consists of different layers. Indium tin oxide (ITO) or Fluorine doped tin oxide (FTO) substrate acts as the transparent conducting cathode. Electron transport layer (ETL) and hole transport layer (HTL) are used to extract and transport charge carriers to the respective electrodes and thus reduce the carrier recombination. The materials TiO_2 , PCBM, ZnO and Al_2O_3 are commonly used as the ETL and Spiro-MeOTAD, PEDOT:PSS and CuI as HTL[12].

PSCs operate on the principle that when light incidents on the device, it reaches into the active layer through the transparent electrode and generates excitons which are dissociated easily into

charge carriers. The binding energy of excitons depends on the optical band gap and the perovskite material. Generated charge carriers have high diffusion length are transported through the transport layers and finally collected by the respective electrodes. In the PSC device with normal structure, electrons are collected by FTO which is the transparent electrode.

It can be understood that most of the hole transport layers introduced in the PSCs were of small molecular type. Copper phthalocyanine (CuPc) is a widely known small molecule metal organic compound that has been commonly used [13] in organic photovoltaic cells as HTL due to its properties such as excellent chemical and thermal stability, flexibility, high hole mobility and its semiconducting property [14]. It has also been introduced in the PSCs [15].

In normal perovskite architecture, HTL is coated on the top of the perovskite surface followed by a layer of a high work function metal as the anode. The HTL facilitates the transfer of holes to anode from the perovskite layer by providing proper band alignment. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the HTL should be greater or lower respectively than that of the perovskite material to provide necessary driving force for the charge transfer process. Certain hole transport materials (HTM) exhibit better performance depending upon the device configuration and the method by which it is fabricated. In normal architecture, if a solution processable HTL is used, it is better to choose HTMs which do not need protic or polar solvents that dissolve the perovskite material. However, the solvent of the HTM should have an affinity[8] towards the perovskite layer surface.

In this work, perovskite solar cell devices with and without an HTL layer (Copper Phthalocyanine) are fabricated with normal architecture. Carrier mobility is then estimated using space charge limited current (SCLC) method.

Experimental Details

Fluorine doped tin oxide FTO/TiO₂ coated glass with a dimension of size of 2.5cmx2.5cm from Solaronix was used for the PSC fabrication without any further cleaning. Here, TiO₂ layer acts as the scaffold for facilitating the perovskite coating. The perovskite film was prepared with CH₃NH₃PbI_{3-x}Cl_x precursor ink purchased from Ossila. The ink was stirred for 2hrs. at 60°C and spin coated at 2000rpm for 30s onto the FTO/TiO₂ coated glass plate to form the absorbing layer and the film was annealed at 90°C for 30mins. The CuPc HTL was deposited by thermal evaporation in the vacuum thermal evaporation coating setup at 10⁻⁵ torr base pressure to form a layer of 10nm thickness. As CuPc has a large π conjugated system, it is not easy to dissolve in commonly used organic solvents and therefore vapor deposition method was preferred to get the film. A quartz crystal was used to monitor the thickness. Finally, the anode Ag was evaporated through a shadow mask in the vacuum unit to form a layer of 100nm thickness.

The electrical characterization of the fabricated devices with the configurations FTO/TiO₂/perovskite/Ag and FTO/TiO₂/perovskite/CuPc/Ag were carried out by Keithley Sourcemeter and Solar Simulator at 100mW/cm².

Results and Discussion

The perovskite solar cell devices with and without CuPc hole transport layer are shown in Fig.3 and Fig. 4 respectively.

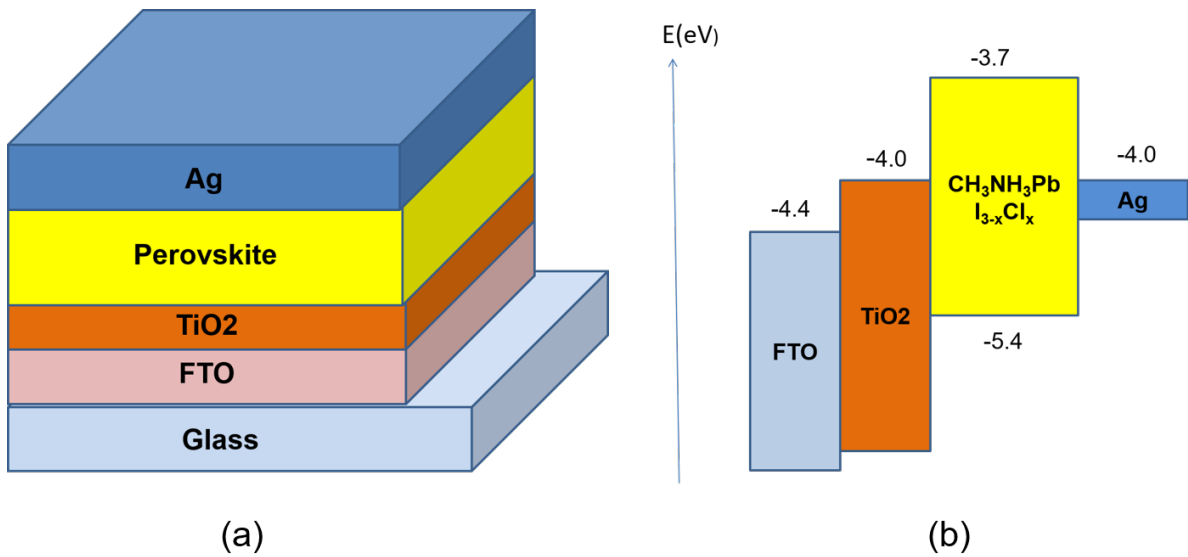


Fig. 3 (a) Perovskite device configuration and (b) Energy level schematic

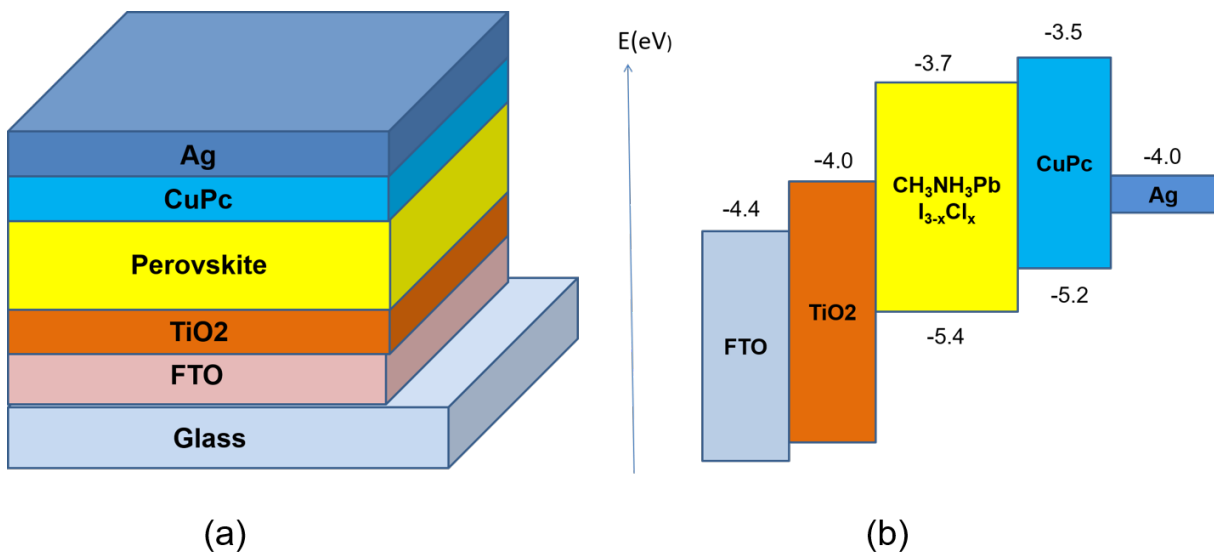


Fig. 4 (a) PSC structure with HTL (b) Energy level of each material

The energy level diagrams of the corresponding device structures are also presented. The working of the PSC depends upon the energy levels of the device layers. When incident light reaches the perovskite active layer CH₃NH₃PbI_{3-x}Cl_x, it excites electrons from HOMO to LUMO energy level by leaving holes in the HOMO energy level [12]. As in Fig. 3(b), the LUMO of CH₃NH₃PbI_{3-x}Cl_x is 3.7eV [15] and the work function of TiO₂ is nearly 4.0 eV, TiO₂ can easily collect the electrons. The copper phthalocyanine coated onto the top of the perovskite film (Fig.4(a)) helps to collect more photogenerated holes by the anode Ag [16]. The energy level of the subsequent layers must have to be matched for the effective functioning of the cell and also provide better contact between the layers.

i)UV-Vis Absorption Characteristics

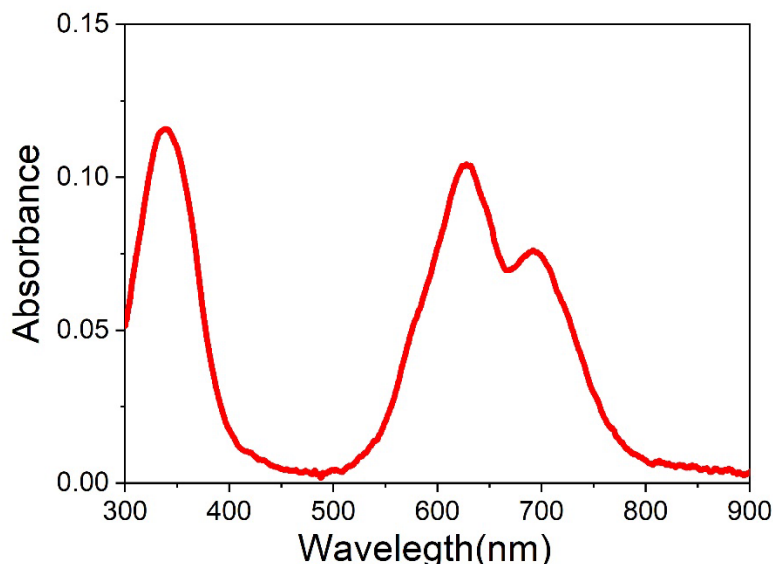


Fig. 5 Absorption spectrum

The optical absorbance spectrum of CuPc (Fig. 5) shows two absorption peaks at about 340nm (UV region) called Soret (B) band and at 625nm (visible region) called Q band. A small shoulder is seen at about 700nm. The Q band that is well known for the phthalocyanine molecule appears in between 550 and 750nm which is in the visible region. Generally, the distinct characteristic peaks in the visible spectral region are interpreted as $\pi-\pi^*$ transition between bonding and antibonding molecular orbitals whereas that in the B band, are interpreted as the lowest allowed $n-\pi^*$ excitation. It can also be noted that the band exhibits Davydov splitting [17] seen in all phthalocyanine derivatives. The high energy and low energy peaks available in the Q band correspond to the first and second $\pi-\pi^*$ excitation[17].

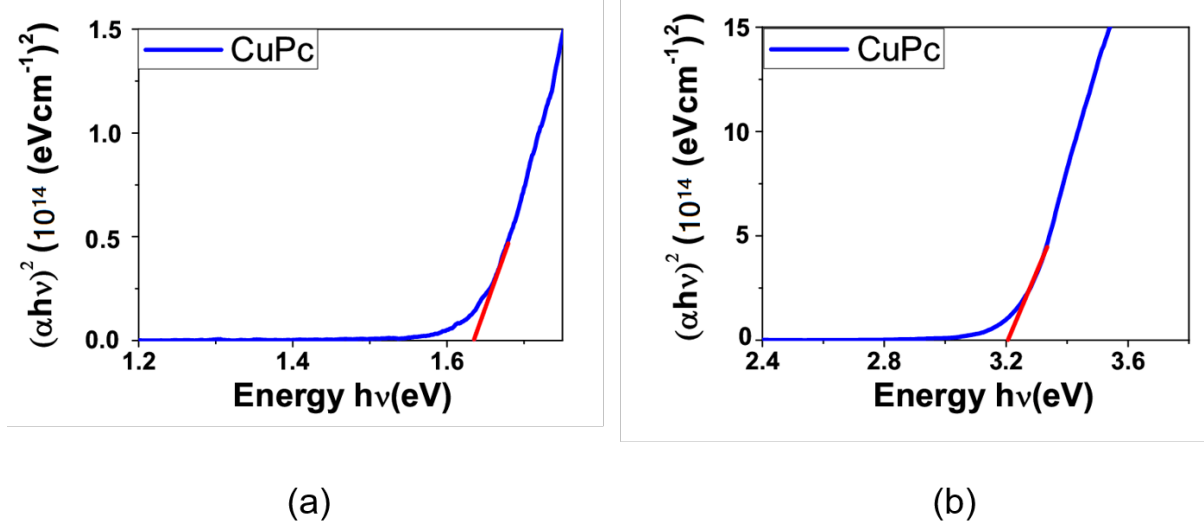


Fig. 6 Tauc's plot for energy band gap calculation

The optical energy gap of CuPc is evaluated from its absorption spectrum near the fundamental absorption edges. In these regions, the incident photon energy $h\nu$ is related to the absorption coefficient α as:

$$\alpha h\nu = B(h\nu - E_0)^m \tag{1}$$

where E_0 is the optical band gap, B is the transition probability which is constant within the optical frequency range and m is transition constant and has values $m=0.5$ for direct and 2 for indirect [18] transitions.

The characteristics of $(\alpha h\nu)^2$ versus $h\nu$ near the Q and B band absorption edges are shown in Fig. 6. The optical band gaps CuPc is determined by extending tangent to zero absorption and are obtained as 1.63eV and 3.2eV.

ii) J-V Characteristics

Carrier mobility is one of the important characteristics of transporting material for effective carrier extraction and transport. The mobility is therefore calculated using the space charge limited current method from the dark characteristics (Fig.7(b)). In the SCLC region, the J-V characteristics become quadratic where the current density depends on mobility rather than the carrier density [19] and therefore the carrier mobility can be evaluated using the relation:

$$J = \frac{9\mu\epsilon V^2}{8d^3} \tag{2}$$

The hole mobility in the device is obtained as $0.0013\text{cm}^2/\text{Vs}$ which is closer to the value reported [8].

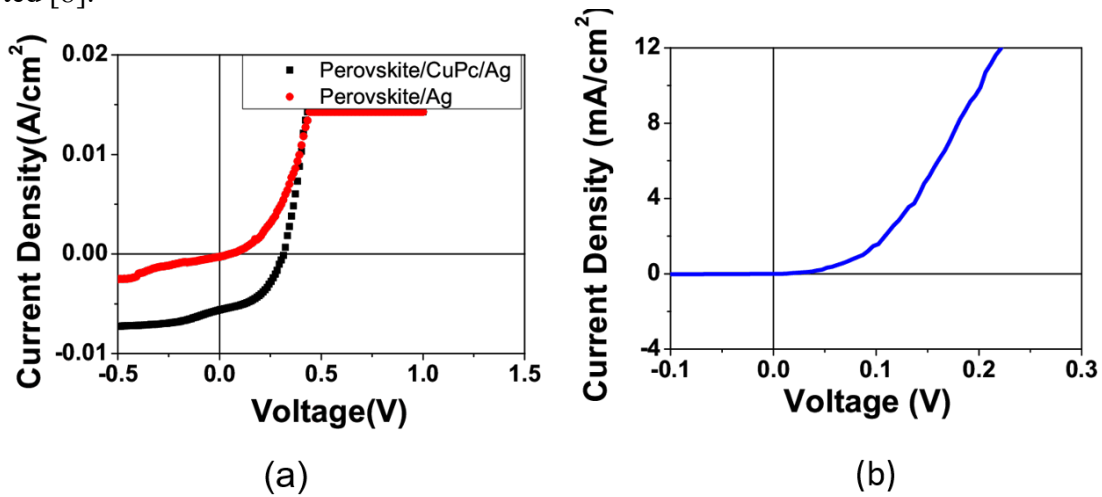


Fig. 7 J-V characteristics (a) illumination (b) dark

Under illumination the current-voltage characteristics of the PSC devices were obtained as in Fig.7(a) and the parameters determined for each cell were presented in Table 1. The device fabricated with CuPc as HTL with an active area of 7mm^2 returned open circuit voltage (V_{oc}) of 0.31V, short circuit current density (J_{sc}) of $6\text{mA}/\text{cm}^2$ and fill factor of 46.11% which resulted in an efficiency of 0.8%. Even though the V_{oc} obtained is of greater with HTL, but it has not reached to the expected value as the HOMO level of CuPc is 5.2eV because the photovoltage of the device is decided by the difference in the quasi Fermi levels [13] of electron and hole conducting materials. The J_{sc} is improved due to the efficient extraction and transport of holes by the CuPc

layer. The higher the hole conductivity of the metal organic combination, the larger values of J_{sc} and FF. The fill factor is also improved due to the small value of series resistance R_s [20].

Table 1 Photovoltaic Parameters of the Perovskite solar cells

Device	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE [%]	R_s [Ω]	R_{sh} [Ω]
Without HTL	0.0225	0.2383	41.99	0.002	221.73	195.69
With CuPc as HTL	0.3130	6.0	46.11	0.80	13.76	204.92

The CuPc absorption spectrum shown in Fig. 5 is not preferably applicable for the normal architecture, but to the inverted one [8]. Usually, a portion of the light is reflected by the metal electrode to the perovskite layer and it can improve the device performance, but in the normal structure, the reflected light would get hold by the CuPc layer.

The PSC devices in this study were fabricated under ambient conditions and humidity. The readings were also taken under the same conditions without encapsulating the devices and this has resulted in uncharacteristically low values of efficiency recorded for the devices studied here. However, as the investigations intended objective is to comparatively study the effect of the CuPc HTL, this limitation may be ignored as the results provided valuable data and insight in achieving the intended objective.

Conclusions

The perovskite solar cell devices in normal architecture were constructed and tested with CuPc hole transport layer. The effect of CuPc was studied and observed that the device performance was enhanced with the introduction of HTL. The parameters J_{sc} and FF were improved due to the higher hole conductivity of the CuPc layer. The device fabrication was carried out under ambient conditions of high humidity, without using a glove box which account for the uncharacteristically poor performance of the devices. But the objective of the study has been accomplished as the results show a much high and unambiguous performance enhancement with CuPc as HTL compared with the device without any interfacial layer. The hole mobility was determined using SCLC method and it was obtained as 0.0013cm²/Vs.

Acknowledgements

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References

- [1] A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells, *J. Am. Chem. Soc.* 131 (2009) 6050-6051. <https://doi.org/10.1021/ja809598r>
- [2] H. J. Snaith, Perovskites : The Emergence of a New Era for Low-Cost , High-Efficiency Solar Cells, *J. Phys. Chem. Lett.* 4 (2013) 3623–3630. <https://doi.org/10.1021/jz4020162>

- [3] H. Kim, C. Lee, J. Im, K. Lee, T. Moehl, A. M Marchoro, S. Moon, R. H. Baker, J. Yum, J. E. Maser, M. Gratzel, N. Park, Lead iodide perovskite sensitised All-Solid-State Submicron Thin Film Mesoscopic solar cell with efficiency exceeding 9%, *Sci. Rep.* 2 (2012) 591-597. <https://doi.org/10.1038/srep00591>
- [4] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, H. J. Snaith, Efficient Hybrid Solar Cells based on Meso -Superstructured Organometal Halide Perovskites, *Science* 338 (2012) 643–648. <https://doi.org/10.1126/science.1228604>
- [5] D. S. Philips, W. Warmuth, Fraunhofer ISE: Photovoltaics Report, 2019.
- [6] Z. Wu, T. Song, B. Sun, Carbon-Based Materials used for Perovskite Solar cell, *ChenNanoMat* 3 (2017) 75-88. <https://doi.org/10.1002/cnma.201600312>
- [7] M. A. Green, A. Ho-baillie, H. J. Snaith, The emergence of perovskite solar cells, 8 (2014) 506–514. <https://doi.org/10.1038/nphoton.2014.134>
- [8] A. Gheno, S. Vedraïne, B. Ratier, J. Bouclé, π -Conjugated Materials as the Hole-Transporting Layer in Perovskite Solar Cells, *Metals* 6 (2016) 21–42. <https://doi.org/10.3390/met6010021>
- [9] W. Chen, Y. Wu, Y. Yue, J. Liu, W. Zhang, X. Yang, H. Chen, E. Bi, I. Ashraful, M. Gratzel, L. Han, Efficient and stable large-area perovskite solar cells with inorganic charge extraction layers, *Science* 350 (2015) 944–949. <https://doi.org/10.1126/science.aad1015>
- [10] Z. Yi, H. Ladi, X. Shai, H. Li, Y. Shen, M. Wang, Will organic – inorganic hybrid halide lead perovskites be eliminated from optoelectronic Applications?, *Nanoscale Adv.* 1 (2019) 1276–1289. <https://doi.org/10.1039/C8NA00416A>
- [11] M. Yokota, K. Fujii, M. Ishigo, K. Sasaki, H. Kato, N. Doki, Enabling Solution Growth of Insoluble Organic Materials in Common Solvents, *Adv. Chem. Eng. Sci.* 6 (2016) 82-86. <https://doi.org/10.4236/aces.2016.62010>
- [12] A. Baron, Synthesis and Characterization of methyl ammonium lead tri halide Perovskite Compounds and their Applications in Photonic Devices, Ph. D, University of Basrah, 2019.
- [13] X. Jiang, Z. Yu, J. Lai, Y. Zhang, N. Lei, D. Wang, L. Sun, Efficient perovskite solar cells employing a solution-processable copper phthalocyanine as a hole-transporting material, *Sci. China* 60 (2017) 423–430. <https://doi.org/10.1007/s11426-016-0393-5>
- [14] J. Zaumseil, H. Sirringhaus, Electron and Ambipolar Transport in Organic Field-Effect Transistors, *Chem. Rev.* 107 (2007) 1296–1323. <https://doi.org/10.1021/cr0501543>
- [15] C. V. Kumar, D. Georgia Sfyri Raptis, E. Stathatos, P. Lianos, Perovskite Solar Cell with Low cost Cu-Phtalocyanne as Hole Transporting Layer, *RSC Adv.* 5 (2015) 3786–3791. <https://doi.org/10.1039/C4RA14321C>
- [16] S. Pitchaiya, M. Natarajan, A. Santhanam, V. Asokan, A. Yuvapragasam, V. M. Ramakrishnan, S. E Palanisamy, S. Sundaram, D. Velayuthapillai, A review on the classification of organic/inorganic/carbonaceous hole transporting materials for perovskite solar cell application, *Arab. J. Chem.* 13 (2020) 2526-2557. <https://doi.org/10.1016/j.arabjc.2018.06.006>

- [17] A. A. M. Farag, Optical absorption studies of copper phthalocyanine thin films, *Opt. Laser Technol.* 39 (2007) 728–732. <https://doi.org/10.1016/j.optlastec.2006.03.011>
- [18] Z. U. Islam, M. Tahir, W.A. Syed, F. Aziz, F. Wahab, S. M. Said, M. R. Sarker, S. H. Md Ali, M. F. M Sabri, Fabrication and photovoltaic properties of organic solar cell based on zinc phthalocyanine, *Energies* 13 (2020) 962-975. <https://doi.org/10.3390/en13040962>
- [19] K. L. Usha Kumary, M. Pratheek, T. A. Shahul Hameed, P. Predeep, Measurement of hole mobility in P3HT based photovoltaic cell using space charge limited current method, *AIP Conf. Proc.* 2162 (2019) 20142–20147. <https://doi.org/10.1063/1.5130352>
- [20] J. Wang, Z. Wang, M. Li, C. Zhang, L. Jiang, K. Hu, Q. Ye, L. Liao, Doped Copper Phthalocyanine via an Aqueous Solution Process for Normal and Inverted Perovskite Solar Cells, *Adv. Energy Mater.* 8 (2018) 1701688- 1701696. <https://doi.org/10.1002/aenm.201701688>