Recent Development in Copper based Hole Transport Materials for Emerging Inverted Perovskite Solar Cells

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Abstract. In the photovoltaic (PV) research community, the dramatic improvement in the power conversion efficiency of organic-inorganic metal halide perovskite-based devices has made them very appealing. The serious challenge, though, has to do with durability under different circumstances and difficulties with toxicity. In recent years, a significant number of papers have been published in PSCs based on these issues through the use of different electron transport materials (ETMs), hole transport materials (HTMs), and Perovskite materials. The hole transport material is responsible for a significant part of the expense of the components of a Perovskite solar cell (PSC), as the most effective systems so far have costly HTMs, such as spiro-OMeTAD and poly(triaryl amine). The inverted PSCs (p-i-n) give a wide variety of alternate HTLs, as the HTL is deposited underneath the perovskite layer. Any material with moderate hole mobility is, therefore, a possible substitute for replacing the expensive HTMs that have been used so far. In this review manuscript, we have compiled the various Cu-based materials added as HTMs in planar inverted p-i-n structure. This manuscript appears to focus on the role and classification of various copper-based materials used as a hole transport layer affecting long-term stability, improving solar cell parameters, and thus improving overall device performance. Furthermore, a description of the overall device structure, preparation methods, and the effect of the thickness of the HTM layers on the overall solar cell parameters of the perovskite devices is also presented. We hope that this analysis will explicitly and extensively demonstrate their significance and strengths in the concerned domain by introducing and exploring the developments of Cu-based materials as HTMs in planar PSCs and provide inspiration for their further development.

1. Introduction
The desire for an environmentally friendly and economically feasible supply of energy has been the driving force for many decades of intensive research aimed at achieving high-efficiency low-cost power generation systems. Photovoltaic cells make it possible to directly transform solar radiation to energy utilizing light absorbers, and recent developments in solar conversion technologies have persuaded many researchers that their pledge may eventually be fulfilled. Since the first study on their application in PV devices, which has established a new field in optoelectronics, organometal halide perovskites have successfully completed ten years in 2020, with consistently rising, extremely impressive performance, both at the material level and also at the corresponding device level. Perovskites became the most intensively investigated material in this area since the Si revolution, with a wide range of optoelectronics applications.
1.1. Crystal Geometry of Perovskite

"Perovskite" originally applies to the crystal structure of calcium titanate found by the mineralogist Gustav Rose in 1839. The term 'perovskite' has been used to attribute to all compounds with the same crystal lattice as calcium titanate. There is a general formula of ABX$_3$ in the perovskite light-absorbing layer, where A corresponds to an organic cation (e.g. CH$_3$NH$_3^+$), B corresponds to metal cation (e.g. Pb$^{2+}$) with the coordination number of 6 and X is the halogen that is chlorine, bromine or iodine or a combination of chlorine, bromine and iodine. There are some excellent properties of the perovskite material like large absorption coefficient, tunable bandgap, solution-based synthesis approach [1]. And because of all these excellent properties, perovskite is a choice the preferred material for making solar cells. Another important aspect of the perovskite is that by changing either the A cation or by X anion or by the M sides. We can tune the bandgap over a wide range keeping the absorption coefficient the same, because of that the optical properties of this material are very very tunable.

Figure 1 corresponds to the molecular arrangement of a perovskite material where M is lying at the center, A is at the corner and the phase center is occupied by the halogen atoms. So the octahedral has been equally shared by each of these unit cells when surrounded by a three-dimensional polymer. This kind of octahedra they are coordinated with each other to make a joint cuboctahedral geometry and the metal cations sits at the center of this cube cuboctahedral geometry.

![Figure 1. Crystal structure of organo metal halide perovskite [2].](image)

1.2. Development in Perovskite Solar Cells (2006-2020)

Perovskite was first introduced as the light-absorbing material reported by Kojima and his team in 2006. To substitute the dye in dye-sensitized solar cells (DSSCs), they deposited MAPbBr$_3$ on mesoporous TiO$_2$ and developed a PV cells with a efficiency of 2.19 %. They substituted MAPbBr$_3$ with MAPbI$_3$ in 2009 and raised the PCE to 3.81% because of the more appropriate bandgap [3].

In the year 2011, Park and his teammate subsequently had a similar device configuration in which the perovskite layer was deposited as quantum dots (QDs). Perovskite QDs reported higher light absorption capabilities Compare to DSSC. A PCE of 6.54 % was obtained by perovskite QDs [4]. Both of the above devices were based on the DSSC structure whose sensitizer has been soaked in Electrolyte liquid. The Perovskite materials should, however, be dissolved into the electrolyte, so the solar cells’ output rapidly deteriorated after it had been prepared. In 2012, when M. Gratzel and his team fabricated PSC devices using perovskite as an absorber layer, and mp-TiO$_2$ and spiro-MeOTAD were used as the electron transport material (ETM) and hole transport material (HTM) respectively, the Perovskite solar cell attracted solar researcher interest. The reported efficiency was 9.7 %[5].
In 2013, by making use of vapor deposition, Liu and his team developed planar heterojunction PSCs, and the efficiency of the PSCs reached up to 15.4%[6]. In 2014, H. Zhou and his team manufactured PCS through ETL doping and ITO Electrode alteration. Results demonstrate that the yttrium doped TiO$_2$ (ETL) strengthens the electron transport channel in the PSC system and raises the concentration of its carrier and modifies the ITO electrode in order to decrease its work function. A PCE of 19.3 % was reached by these changes [7].

Formamidinium (FA) had been used to accurately change the band gap to balance the sunlight spectrum as a substitute or selective supplement of methylamine (MA). The intramolecular exchange procedure was used by the SangSeok group in 2015 to deposit mixed-cation perovskite film and obtain perovskite with complete morphology[8]. The mixed-cation perovskite film-based device yielded a PCE of 20.1 %, which was more than 20 percent of the PCE’s first study. To improve the temperature stability of the perovskite, the Gratzel and his team in the year 2016 inserted the cesium element into the mixed-cation perovskite film and obtained the unit with a stabilized PCE of 21.1 %[9]. In 2017, using the contact passivation technique, Sargent and his team obtained an efficiency of 20.1 % [10]. Kim and his team stated in the same year that the injection of additional iodide ions into the organic cation solution lowered the concentration of deep-level defects. The PSC-certified PCE achieved 22.1 %[11]. The National Renewable Energy Laboratory (NREL) recorded a PCE of 23.7% in 2018 [12]. As of now verified efficiency of 24.8% is reported by Mingyu Jeong and his team in September 2020. Figure 2 shows the overall development of perovskite solar cell till date [13].

2. Classification of Copper based Hole Transport Materials
Among the other inorganic materials that are currently at the centre of the research as alternative HTLs, copper-based materials have provided the most promising results so far. Materials based on copper have been used for several years in photo-electrochemical devices. Compared to other inorganic HTMs, their key benefit is their large variety of combinations, resulting in innovative materials that can be fabricated at low temperatures and low-cost techniques, having the chance to scale up. The hole transporting materials based on Cu has shown great potential because they give fascinating characteristics, such as sufficient band alignment with the perovskite, high mobility of the hole, and ability to fabricate using solution process methods. In addition, although p-type dopants, like salts relying on Cobalt and lithium, are widely used as additives to increase conductivity in organic HTMs, these are highly hygroscopic and thus affect the stability
of the devices. Besides being non-hygroscopic, Cu-based materials have high conductivity, which enables them powerful even without the addition of dopants. Classification of various copper based HTMs used in inverted perovskite solar cell is depicted in Figure 3.

Figure 3. Classification of HTMs based on copper

2.1. Oxide of Copper as a HTMs(Cu$_2$O/CuO/CuOx)

Chuantian Zuo and team performed an experiment with the suggested p-i-n based system configuration. ITO–Cu$_2$O / CuO –MAPbI$_3$–PC$_{61}$BM–Ca–Al. An innovative method called the facile method is adopted for producing Cu$_2$O and CuO films [14]. First of all copper iodide is treated with NaOH(aq) to produce Cu$_2$O Film and then CuO layer was produced by air heating, as represented by equation 1-2.

\[
\begin{align*}
CuI + NaOH & \rightarrow Cu_2O + NaI + H_2O \\
Cu_2O + O_2 & \rightarrow CuO
\end{align*}
\]

Experiments have shown good-crystallized MAPbI$_3$ on the Cu$_2$O and CuO crests. Unlike PEDOT cells, this contributed to a major increase in open-circuit voltage, short circuit current, and PCE. The PCE registered by Cu$_2$O and CuO cells was 13.35% and 12.16% respectively. For more stability research, after the elimination of the Ca coating, the concocted unit was mounted in the air. The inference that came was surprising. For Cu$_2$O based PSC, PCE deteriorate only 10% of starting value after 70 days.

Lung-Chieh Chen and his team experimented with the reported configuration ITO–CuO-Cu$_2$O–CH$_3$NH$_3$PbI$_3$– C$_{60}$|BCP–Ag [15]. In order to perform the experiment, a nano-configured CuO- Cu$_2$O based PSCs was concocted. To deposit the CuO- Cu$_2$O layer, air aided heating was used. The Cu thin film deposited in this process was heated in the presence of air at 300-400 °C. The concentration of the hole and the mobility of the hole were seen to increase by increasing the temperature. At 60 nm thick CuO-Cu$_2$O at 350 °C, the maximum registered PCE was 8.1%

Soumyo Chatterjee and his team recorded more improvements in productivity in the same year. Utilizing Successive Adsorption and Reaction of Ionic Layer (SILAR) method to deposit Cu$_2$O layer over TCO substrate [16]. Reduced energy loss and surface recombination between perovskite and Cu$_2$O and increased perovskite film crystallinity on Cu$_2$O were observed. The unit made up of TCO– Cu$_2$O –Perovskite–PCBM–Al obtained a efficiency of around 8.2% using CH$_3$NH$_3$PbI$_3$ as the absorber layer and 8.30% by using MAPbI$_{3-x}$Cl$_x$ as the perovskite material.

Lan Liu and his group proposed the concept of the HTL free perovskite composition. Electrodeposited Cu$_2$O on the ITO base was used to establish the sites for perovskite [17]. The above approach was found to introduce mediated homogeneity and perovskite crystallization. Due to direct ITO and perovskite interaction, open-circuit voltage and fill factor became
retarded. The structure ITO – Cu$_2$O – sequential deposited MAPbI$_3$ – C$_{60}$ – Bphen – Ag obtained a PCE of 9.64%.

Again, another experiment was carried out by the team headed by Weili Yu in 2016 to increase the overall efficiency of the system. The fabrication was performed using the device structure made of ITO – Cu$_2$O – d MAPbI$_3$ – PCBM – Ag [18]. Economical simple thermal oxidation, the Cu$_2$O layer was formed. The result obtained was better carrier lifetime and good band positioning with perovskites. The thickness of the Cu$_2$O layer control system output was demonstrated. The recorded optimum PCE was 11.03% at a 5 nm thick Cu$_2$O layer.

In the year 2016, an experiment was performed by Weihai Sun et al. to implement the specified system configuration: ITO – CuO$_x$ – MAPbI$_3$ – C$_{60}$ – BCP – Ag [19]. For the CuO$_x$ layer, the inexpensive, simple solution-processed technique of ozone treatment was implemented. It was observed that the improvement in device output was due to the rapid movement of the carrier from the perovskite to CuO$_x$. The optimum recorded PCE was with reduced hysteresis at 17.1%. The device showed improved reliability even after 200 hours in the air, and 90% of its original PCE was retained by the device. The performance was astonishing and closer to standards.

Haixia Rao and his team have announced a significant breakthrough in overall product performance [20]. To create a perovskite base, the modified one-step rapid deposition-crystallization process was implemented. The policy adopted was a new doping action plan. To produce hybrid perovskite, Cl is treated with MAPbI$_3$. There has been progressing in resistance to system recombination, hole stability, and morphology. For the system configuration composed of ITO – CuO$_x$ – MAPbI$_3$ – x Cl – x PCBM – C$_{60}$ – BCP – Ag, the maximum reported PCE was 19%.

In 2017, in order to research the properties of charge accumulation, Galatopoulos and team modeled a PV cell with a CuO-coating as hole transport layers (HTL). The system inverted was made up of ITO – CuO – MAPbI$_3$ – PC$_{70}$BM – AZO – Al [21]. The charge set has been studied with HTL/Perovskite interfaces by spectroscopy and frequency capacitance analysis to correlate the efficiency of the system. The study noted that there has been a rise in the sum of J$_{SC}$ due to efficient hole extraction in CuO-based systems. In addition, the metal halide perovskite showed elevated grain of size around 630 nm on CuO HTL with a decreased number of grain limits. The decreased grain frontiers increased the resistance of recombinations and the maximum PCE reported was 15.3%.

In 2019, Savva and the team used CuAlO$_2$(77 %)/CuO(23 %) as a HTM to produce ITO – [CuAlO$_2$ – CuO](77:23) – MAPbI$_3$ – 70% PCBM – 30% AZO – Al was the system set up that followed [22]. In order to prepare CuAlO$_2$ / CuO, flame spray pyrolysis was used and its dispersions were treated with high-frequency sonication. This method transforms large agglomerates into tiny particles of CuAlO$_2$/CuO. By way of centrifugation, the residual large particles are stopped from dispersion. This group’s reported PCE was 16.3% with almost no hysteresis.

2.2. Sulphide of Copper as a HTMs(CuS)

By utilizing CuS Nanoparticles(NP) as a hole transport layer, Rao and his team have achieved a decent efficiency. On the system setup, the evaluation was performed on ITO – CuS – MAPbI$_3$ – C$_{60}$ – BCP – Ag [23]. The CuS layer has been deposited with the spin coating technique. A shift in band alignment (–4.9eV to –5.1eV) was observed and it was revealed that HTL and perovskite (–5.4eV) were well disposed of. Spin coating time was an important part of the efficiency of the system. In the optimized spin coating time of the CuS NPs, PCE of 16.2% was recorded by this group.
2.3. Iodide of Copper as a HTMs (CuI, Cu@CuI)

The study of Tian and the team in 2015 was one of the first studies on inverted PSCs, incorporating CuI as the HTL, with positive results. This research has used a cost-effective solution-processed approach to produce hydrophobic CuI layers to replace PEDOT:PSS with FTO−CuI−MAPbI$_3$−PCBM−Al structures in inverted planar PSCs. The use of CuI as HTL, a little above the PEDOT:PSS derived module of 13.28% under the same experimental conditions, obtained a power-conversion efficiency (PCE) of 13.58%. In comparison, Copper iodide based devices displayed increased air stability relative to devices using PEDOT: PSS as hole transport materials.

In 2019, Jing Cao and his coworker performed an experiment combining the hybrid nanostructure of Cu@CuI as a hole transport material [24]. Configuration of the unit was an ITO−Cu@CuI−CsFAMAPb(BrI)$_3$−PCBM−ZnO−Ag. Several big observations ended the experiment. Enhanced functional conductivity, charge transfer properties, and marginal hysteresis was demonstrated by the CuI coated on Cu. Internal Cu helps in the collection of rapid charges produced by surface CuI. Performance of the Champion unit is achieved responding to multi perovskite cations (CsMAFA). The PCE that this community registered was 18.8%.

| Year | HTM | Perovskite | HTM Thickness | $V_{oc}$ (V) | $J_{SC}$ (mA/cm$^2$) | FF (%) | PCE (%) | Ref |
|------|-----|------------|---------------|-------------|---------------------|--------|--------|-----|
| 2015 | Cu$_2$O | MAPbI$_3$ | 10-20 nm | 1.07 | 16.52 | 75.51 | 13.35 | [14] |
| 2015 | CuO | MAPbI$_3$ | 10-20 nm | 1.06 | 15.82 | 72.54 | 12.16 | [14] |
| 2016 | CuO-Cu$_2$O | MAPbI$_3$ | 60-nm | 0.96 | 14.40 | 58.61 | 8.1 | [15] |
| 2016 | Cu$_2$O | MAPbI$_3$ | - | 0.89 | 16.52 | 56 | 8.23 | [16] |
| 2016 | Cu$_2$O | MAPbI$_3$ | - | 0.92 | 15.60 | 58 | 8.30 | [16] |
| 2016 | Cu$_2$O | MAPbI$_3$ | 1.5µm | 0.88 | 18.03 | 61 | 9.64 | [17] |
| 2016 | Cu$_2$O | MAPbI$_3$ | 5-nm | 0.95 | 17.5 | 66.2 | 11.03 | [18] |
| 2016 | CuOx | MAPbI$_3$ | - | 0.99 | 23.2 | 74.4 | 17.1 | [19] |
| 2016 | CuOx | MAPbI$_3$ | 20-35 nm | 1.03 | 22.42 | 76 | 17.43 | [25] |
| 2016 | CuOx | MAPbI$_3$ | - | 1.11 | 22.5 | 75.8 | 19.0 | [20] |
| 2017 | CuO | MAPbI$_3$ | 15-nm | 1.09 | 18.2 | 77 | 15.3 | [21] |
| 2019 | CuAlO$_2$/CuO(77:23) | MAPbI$_3$ | 30-70 nm | 1.07 | 19.1 | 79.6 | 16.3 | [22] |
| 2019 | Cu@CuI | CsFAMAPb(BrI)$_3$ | 15-nm | 1.17 | 22.8 | 80 | 18.8 | [24] |

2.4. Copper Cyanates as a HTM (CuSCN and Passivated CuSCN)

The most important element used frequently in organic and perovskite PV device is copper thiocyanate (CuSCN). As per the current criteria for solar photovoltaic, it shows outstanding characteristics. High hole mobility has been seen as there is a lack of copper atom in its crystal structure. The expanded band difference demonstrated greater UV, near-infrared, and visible spectrum illumination.

In the year 2014, Subbiah and his group first documented the use of Copper thiocyanate (CuSCN) as a hole transporting layer in inverted photovoltaic devices. The result was not really good since PCE was only registered at 3.8% [26]. It was not well suited for the thickness of multiple components, leading to increase in series resistance and decrease in shunt resistance. It was not well suited for the thickness of multiple components, leading to increased series resistance and small shunt resistance. In the same year the same, compared to organic PEDOT: PSS, K Zhao, and his group fabricated solar cell using liquid processed CuSCN as a HTL, showing
greater light absorption of lower wavelengths signals [27]. PSCs made up of ITO—Solution Processed CuSCN – MAPbI$_3$–PC$_{60}$BM–LiF hit achieved a PCE of 10.8%.

The experiments to reach new high efficiency and stability led to many experiments by various groups in order to meet the goal. S.Ye and co-worker reported the CuSCN based PSCs in the year 2015. ITO—CuSCN – MAPbI$_3$(OneStep)–C$_{60}$–BCP–Ag was the system design that proceeded [28]. The perovskite film was formed in this experiment, incorporating a single-step rapid deposition crystallization technique. Using the traditional one-step deposition process, the perovskite solution in Dimethyl formamide (DMF) was then spin-coated. Chlorobenzene was applied to it very rapidly for rapid crystallisation after some time. Surface resistance and surface roughness were minimized by this process. At 16.6%, the champion PCE was registered.

Nilushi Wijeyasinghe and his colleagues focused on further changes in PCE effectiveness in the year 2017 [29]. In order to improve hole extraction capabilities of copper thiocyanate, this team suggested a new solution. The layout of the system was pursued as ITO – CuSCN – MAPbI$_3$– NH$_3$(aq) – PCBM – LiF – Ag. Alkyl sulfide solvents were substituted with watery ammonia to prepare the hole transport layer. In this phase, an ultra-thin layer of CuSCN with a large bandgap was observed. Compared to traditional diethyl sulfide (DES) solutions, the hole mobility was elevated fivefold. The surface roughness was lower for refined CuSCN, which helped to planarize the ITO anode. This group reported an optimal PCE of 17.5%, leaving S. Ye and his team behind them, who had reported a high PCE of 16.6%.

Mei Lyu and his team performed an experiment in 2019 that processed CuSCN as a hole transport substrate, adding potassium thiocyanate(KSCN) as a fine film. With the exception of the hole transport layer, the system configuration used was retained to be similar to that used in Nilushi Wijeyasinghe and team [30]. The main result of the experiment was that when CuSCN was treated with KSCN, the photocurrent density increased. In enhancing photovoltaic parameters, the thiocyanate anion function was crucial. CuSCN film processed by KSCN demonstrated faster Photoluminescence decay time, suggesting a rapidseparation of charge. 14.73% was the PCE registered by this group.

2.5. HTM based on Copper iodide coordinated with thiourea derivatives (Cu(Tu)I)

A decline of trap states was accomplished by Senyun Ye and his team in the year 2017. The copper thiourea iodide was introduced into HTL and the experimental findings were very positive. The setup of the system is ITO–Cu(Tu)I– MAPbI$_{3-x}$Cl$_x$–C$_{60}$–BCP–Ag are designed [31]. Senyun Ye et.al finds that there is a lot of need for the preparation of various layers in the low-cost traditional solution process. It showed that Cu(Tu)I passivate the active perovskite layer trap sites by halide anions and under-coordinated cations. The energy level transition of the trap states took place as seen in Fig. 4. Due to the increase in depletion distance of P-I bulk heterojunction, the increase in hole transport capacities and decline in the recombination of charge carriers occurred. The highest PCE registered was 19.9%.

![Figure 4. Trap state passivation using Cu(Tu)I[31].](image-url)
2.6. HTM based on thiophosphates derivatives of Copper(Cu$_3$PS$_4$)

Xinxing Yin and his colleagues performed an experiment in the year 2019 that used nanoparticle materials as hole transfer materials [32]. As mentioned here, these nanomaterials are used in the inverted p-i-n Perovskite configuration: glass coated with FTO− Cu$_3$PS$_4$ − MA$_{0.7}$FA$_{0.3}$PbI$_3$ − PCBM − BCP − Ag

The tests performed by Yin concluded that Cu$_3$PS$_4$ has the lowest effective holes weight in contrast to the other materials used to carry holes. The optimal band location was illustrated in Fig. 5. The valence band is -5.05 eV, which is well-disposed for holes to be removed completely.

The result shows that the nanoparticle assists the active layer in large grain((MA$_{0.7}$FA$_{0.3}$PbI$_3$)) as shown in Fig. 5. The average PCE was registered at 18.17%. During forward and reverse scans, the test suggested minor hysteresis.

2.7. HTM based on Copper phthalocyanine (CuPc)

The aromatic, strongly blue-green heterocyclic material is phthalocyanine. Its configuration is analogous to those of four fused benzene rings in porphine [33].

By using the method of an aqueous solution processing, Wang and coworker have prepared Cu phthalocyanine-3,4’,4”,4” composite films-tetra sulfonated acid tetrasodium salt (TS-CuPc), dopped with tetra fluoro tetra cyano quino dimethane (F4-TCNQ) with enhanced film conductivity and mobility of the hole. These films were then inserted into the p-i-n inverted structure, which achieved efficiencies of 16.14%, increasing both current density and open-circuit voltage.

In comparison, the TS-CuPc: F4-TCNQ-based system showed better stability than PEDOT: PSS based device. Storing after 350 h, the PCE of TS-CuPc: F4-TCNQ based unit retained 88% of the original PCE in the air at room temperature. The PCE of the PEDOT: PSS-based unit, on the other hand, was easily reduced by half. However, in the composition of organometallic HTMs, such as CuPc, the presence of transition metals is a major concern since these elements can lead to toxicity and carcinogenicity, which can ultimately cause health issues. Furthermore, unmodified CuPc’s low solubility in the most popular organic solvents limits its use in PSCs that are solution-processable.
Table II. Solar cell performance parameters using Copper thiocyanate, thiophosphates and phthalocyanine as a HTMs.

| Year | HTM | Perovskite | HTM Thickness | \( V_{oc} \) (V) | \( J_{SC} \) (mA/cm²) | FF (%) | PCE (%) | Ref |
|------|-----|------------|---------------|----------------|-------------------|--------|---------|-----|
| 2014 | CuSCN | MAPBI\(_{3−x}\)Cl\(_{x}\) | 200-600 nm | 0.9 | 14.8 | - | 3.8 | [26] |
| 2015 | Processed CuSCN | MAPbI\(_3\) | 13-nm | 1.07 | 15.78 | 63.72 | 10.8 | [27] |
| 2015 | CuSCN | MAPbI\(_3\)(OneStep) | 55-59 nm | 1 | 21.9 | 75.8 | 16.6 | [28] |
| 2017 | CuSCN | MAPbI\(_3\) | 3-5 nm | 1.10 | 22.7 | 71 | 17.5 | [29] |
| 2017 | Cu(Tu)I | MAPbI\(_{3−x}\)Cl\(_x\) | - | 1.13 | 22.3 | 78.9 | 19.9 | [31] |
| 2019 | \( Cu_3PS_4\) | MA\(_{0.7}FA_{0.3}\)PbI\(_3\) | 20-nm | 1.069 | 20.83 | 81.6 | 18.17 | [32] |

Table III. Charge transporting materials(hole and electron) with deposition methods of hole transport layer.

| HTM | ETM | HTM Deposition Method | Ref |
|-----|-----|-----------------------|-----|
| \( Cu_2O \) | PC\(_{61}\)BM | Facile Method | [14] |
| \( CuO \) | PC\(_{61}\)BM | Facile Method | [14] |
| \( Cu_2O \) | PCBM | SILAR Technique | [16] |
| \( Cu_2O \) | C\(_{60}\) | Electrodeposition | [17] |
| \( Cu_2O \) | PCBM | Facile thermal oxidation | [18] |
| \( CuO-Cu_2O \) | C\(_{60}\) | Magnetron Sputtering | [15] |
| \( Cu_2O \) | PCBM | SILAR Technique | [16] |
| \( CuOx \) | C\(_{60}\) | Ozone treated Facile Method | [19] |
| \( CuOx \) | PC\(_{61}\)BM | Spin Coating | [25] |
| \( CuOx \) | PCBM | Spin coating | [20] |
| \( CuO \) | PC\(_{70}\)BM | Spin Coating | [21] |
| \( CuAlO_2-CuO\) | PC\(_{70}\) BM | flame spray pyrolysis | [22] |
| \( Cu@CuI \) | PCBM | Spin Coating | [24] |
| \( CuSCN \) | C\(_{60}\) | Electrodeposition | [28] |
| \( CuSCN \) | PCBM | Spin-Casting | [29] |
| \( Cu(Tu)I \) | C\(_{60}\) | Spin Coating | [31] |
| \( Cu_3PS_4\) | PCBM | Spin Coating | [32] |
| \( CuSCN \) | PCBM | Electrodeposition | [26] |
| Solution Processed CuSCN | PC\(_{61}\)BM | Spin Coating | [27] |

3. Conclusion
In this article, we reviewed the new developments in copper-based hole transport materials and their implementation in PSCs with inverted (p-i-n) structure. The current work in this area is rising continuously and several new production methods and material compositions are seen. This is due to the extraordinary properties of the materials, coupled with the simplicity of processing electrodes, by solution-based techniques that apply to large-area applications. A study of data from different papers reveals that Cu derivatives can achieve PCE comparable with standard organic HTMs that have been integrated so far. It also showed higher stability at a minimized expense. In addition, the energy levels can be well-tuned to conform to all
the different constitutions of the Perovskite. The device structure made up of ITO−Cu(Tu)I−MAPbI$_3$−xCl$_x$−C$_60$−BCP−Ag demonstrated the highest PCE of 19.9% among the different Cu-based HTMs. For solar cell applications, they are well known as effective p-type semiconductors, producing elevated photovoltage values. The efficiency of most of the devices reviewed so far is very ordinary, and if the study on such HTMs is pursued, there is a chance of more extraordinary feats. Close analysis of experimental results suggest that there is huge potential in HTMs like CuAlO$_2$, CuO, CuO$_x$, and Cu@CuI.

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