Progress on the Synthesis and Application of CuSCN Inorganic Hole Transport Material in Perovskite Solar Cells

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Abstract: P-type wide bandgap semiconductor materials such as CuI, NiO, Cu₂O and CuSCN are currently undergoing intense research as viable alternative hole transport materials (HTMs) to the spiro-OMeTAD in perovskite solar cells (PSCs). Despite 23.3% efficiency of PSCs, there are still a number of issues in addition to the toxicology of Pb such as instability and high-cost of the current HTM that needs to be urgently addressed. To that end, copper thiocyanate (CuSCN) HTMs in addition to robustness have high stability, high hole mobility, and suitable energy levels as compared to spiro-OMeTAD HTM. CuSCN HTM layer use affordable materials, require short synthesis routes, require simple synthetic techniques such as spin-coating and doctor-blading, thus offer a viable way of developing cost-effective PSCs. HTMs play a vital role in PSCs as they can enhance the performance of a device by reducing charge recombination processes. In this review paper, we report on the current progress of CuSCN HTMs that have been reported to date in PSCs. CuSCN HTMs have shown enhanced stability when exposed to weather elements as the solar devices retained their initial efficiency by a greater percentage. The efficiency reported to date is greater than 20% and has a potential of increasing, as well as maintaining thermal stability.

Keywords: perovskite solar cells; hole transport materials; inorganic hole transport materials; CuSCN

1. Introduction

We have recently witnessed the rise of perovskite solar cells (PSCs) based on organic–inorganic halide perovskites as the next generation of thin-film solar cells. They have managed to rise above their predecessors, dye-sensitized solar cells (DSSCs) from an efficiency of 3.8% to 23.3% in less than 10 years of research [1–3]. The keen interest in PSCs and their exceptional performance can be attributed to the excellent properties of the perovskite light absorbers which include long diffusion lengths, defect tolerance, strong absorption coefficient, low recombination rates, ease of fabrication and high charge mobility as well as favorable bandgaps [4–6]. However, commercialization of PSCs has been limited due to stability, carrier lifetime and current-voltage hysteresis issues [7]. Perovskite materials are known to degrade when exposed to moisture, heat, oxygen and UV radiation. Consequently, research efforts are now focused on improving the stability and cell performance issues of PSCs to pave way for commercialization.

The PSC is made up of an active perovskite layer, an HTM, an electron transport material (ETM), a back electrode, a transparent electrode and or a mesoporous TiO₂ layer. Figure 1 presents the schematic diagrams of the mesoscopic and planar PSC device architecture.
The low efficiency was as a result of the perovskite material dissolving in the tri-iodide redox couple (I$_3^−$/I$^−$) employed in DSSCs and achieved an efficiency of 3.8% [9]. The low efficiency was as a result of the perovskite material dissolving in the tri-iodide redox couple electrolyte. Even though the use of spiro-OMeTAD led to improved performance, spiro-OMeTAD suffers from low hole mobility of about $6 \times 10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ and low electrical conductivity in its pristine state. In order to improve the performance of spiro-OMeTAD, additives such as Li-TFSI lithium bis (trifluoromethanesulfonylimide) and silver bis (trifluoromethanesulfonylimide) (AgTFSI) have been commonly adopted [10,11]. However, the use of these additives resulted in the degradation of the perovskite layer, thus leading to long-term PSCs instability. Moreover, use of spiro-OMeTAD as HTM in PSCs present several limitations as it is costly to manufacture and the synthesis routes are tedious which does not augur well for large-scale fabrication, thus making it not viable for commercial production [10,11]. Therefore, research efforts have been dedicated to finding alternative HTMs of improved stability and hole mobility as they have a significant contribution to the performance of PSCs [12]. Since the introduction of spiro-OMeTAD, various organic HTMs such as PEDOT:PSS (poly(3,4-ethylenedioxythiophene)-poly (styrenesulfonate)), PTAA (poly(triarylamine)), triphenylamine-based molecules (TPA), carbazole-based molecules, spiro-OMeTAD derivatives and thiophene-based molecules have been tested in PSCs [13–15]. All these research efforts were centered at finding affordable HTMs with improved hole mobility, stability, and a feasible synthesis route.

![Figure 1. Different PSC device architecture (a) Inverted mesoscopic (p-i-n) device (b) Inverted planar (p-i-n) device (c) Mesoscopic (n-i-p) device (d) Planar (n-i-p) device.](image-url)
In addition to organic HTMs, inorganic HTMs such as CuI, CuSCN, NiO, and Cu$_2$O which potentially have better stability than organic HTMs have also been tested in PSCs [16–18]. Christians and co-workers [19] were the first to apply inorganic HTM materials in PSCs. They fabricated copper iodide (CuI) on regular-structured PSC and obtained a conversion efficiency of 6% with low open-circuit voltage ($V_{OC}$) of 0.79 V that was due to high recombination levels. The PCE of the CuI-based HTM swiftly reached 16.8% in inverted planar architecture [20]. Inherent advantages, such as the ability to reduce the production costs, suitable energy levels, high hole mobility as well as enhancement of its resistance to degradation, make inorganic HTMs a promising class of materials to replace spiro-OMeTAD [21,22]. In addition, the stability of PSCs has been improved by inorganic HTMs and the conversion efficiency has rapidly increased in the past few years [23]. However, it has been reported that most solvents used for inorganic material deposition dissolve the perovskite materials, and this could be the reason why there is a dearth of scientific reports that report on applications of inorganic HTMs in PSCs. One such promising inorganic HTM is CuSCN, which is an inexpensive and abundant metal pseudohalide of singly ionized copper. It has a well-aligned work function and has demonstrated high mobility as well as good thermal stability [24]. Therefore, this review is focused on reporting the progress of CuSCN inorganic HTMs. This review also discusses the various fabrication routes employed up to date to prepare CuSCN-based PSCs. This review paper also evaluates the photovoltaic performance of the tested solar cell devices employing CuSCN HTMs. Lastly, the review paper presents the various architectures employed in the PSCs. The triumphs and challenges of the CuSCN HTMs in PSC are presented here in detail.

2. Roles and Ideal Characteristics of HTM

Hole transport materials play different crucial roles, such as: (i) blocking electron transfer to the back-contact metal electrode, (ii) extraction of photo-generated holes from the perovskite and transportation of these extracted charges back to the back-contact metal electrode, and (iii) prevent direct contact between the metal electrode and the perovskite layer [25–29]. An ideal HTM should exhibit properties, such as: (i) high hole mobility, chemical stability and thermal robustness to withstand annealing process during fabrication of the PSC; (ii) the highest occupied molecular orbital (HOMO) energy level should match the valence band energy of the perovskite; (iii) should protect the perovskite layer from air and moisture and be able to prevent the diffusion of external moieties or elements inside the photo-absorber. Moreover, the HTM should have a low annealing temperature and short annealing times to avoid degradation of the underlying layers. Last but not least, the HTM (iv) should show minimum absorption in the visible and near-infrared of the solar spectrum to avoid absorption of photons during the photo-excitation of excitons [29–33].

CuSCN has received significant attention as an HTM in PSC due to the fact that it has a higher maximum hole mobility of about 0.1 cm$^2$ V$^{-1}$ s$^{-1}$ which is far larger than of spiro-OMeTAD with a maximum hole mobility of 6 × 10$^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$. Moreover, CuSCN HTM has suitable energy levels (Figure 2) as well as affordable and simplified synthesis routes as compared to spiro-OMeTAD which makes it ideal for large-scale applications. In light of these observations, this review paper will focus on the recent progress of CuSCN HTM in PSCs.
properties of CuSCN are due to Cu 3d orbital with some hybridization from the S 3p orbitals near the valence band edge. Additionally, CuSCN can be modified easily due to its quasi-molecular property resulting in new materials with different properties [38]. This makes CuSCN a material of choice for various optoelectronic applications.

3. Synthesis and Deposition of CuSCN HTM

Copper thiocyanate is a p-type semiconductor with appealing characteristics such as a wide band gap of 3.6 V, high hole mobility of 0.01–0.1 cm² V⁻¹ s⁻¹, high transparency, and high chemical stability [36]. CuSCN exists in α- and β-phase, with the structures given in Figure 3. It has been reported that β-phase is more stable and is easily accessible. The α- and β-phase can be classified as orthorhombic and hexagonal or rhombohedral structure, respectively [37]. Unlike other inorganic HTMs such as Cu₂O, NiO and SnO, CuSCN is an efficient hole injection/extraction material as well as an electron blocking material due to its appropriate electronic levels. The excellent hole transporting properties of CuSCN are due to Cu 3d orbital with some hybridization from the S 3p orbitals near the valence band edge and the π* antibonding orbital from the cyanide portion near the conduction band edge. Additionally, CuSCN can be modified easily due to its quasi-molecular property resulting in new materials with different properties [38]. This makes CuSCN a material of choice for various optoelectronic applications.

CuSCN has been used in quantum dot-based light-emitting diodes [39], organic light-emitting diodes [40] and transparent thin-film transistors, and has yielded exceptional results [41]. Due to the simplified, affordable and straightforward techniques used to fabricate CuSCN HTMs, PSCs
employing CuSCN HTMs have a greater opportunity to reach the commercial markets as compared to PSCs employing spiro-OMeTAD as HTM.

To that end, simple deposition techniques such as doctor blading, spin coating, spray coating, and electrodeposition have been used in depositing CuSCN HTMs [42–44] which augur well with the commercialization of these devices. However, it has been reported that solvent selection for solution-based deposition methods plays a crucial part in the overall photovoltaic performance of PSCs employing CuSCN HTMs. Polar solvents, such as ethyl sulfide, dipropyl sulfide, and diethyl sulfide [45–47] have been used in the deposition of CuSCN HTMs, with dipropyl sulfide being the most widely used. The use of a wide range of solvents is very limited in case of CuSCN as it is only soluble in polar solvents. However, these polar solvents tend to dissolve the perovskite layer as well, which results in very thin perovskite layers and, consequently, lowers the power conversion efficiency (PCE). Qin et al. [48] used doctor blading to deposit CuSCN using dipropyl sulfide solvent. A film thickness of 600 nm was reported and there was some evidence of dissolution of the perovskite on the CuSCN. A PCE of 12.4% was exhibited by the CuSCN-based PSC, with a $V_{OC}$ of 1.016 V and short-circuit current density ($J_{SC}$) of 19.7 mACm$^{-2}$. The number of deposition cycles did not have an effect on $V_{OC}$ and $J_{SC}$ however, it led to an improved FF. In a move to reduce the dissolution of the perovskite layer in the HTM, Sepalage et al. [49] applied a chlorobenzene protective layer on the perovskite prior to deposition of CuSCN by doctor blading. The PSC exhibited a PCE of 9.6% which to the best of our knowledge is the highest achieved to date in a planar (n-i-p) CuSCN-based PSC device. The doctor blading method involved wetting the perovskite layer with chlorobenzene prior to depositing the CuSCN in dipropyl sulfide. This resulted in the formation of a thick uniform CuSCN film. Whilst the device without the chlorobenzene buffer resulted in relatively thin films as shown here in Figure 4. Figure 4, clearly shows that dissolution of the perovskite layer occurs when only dipropyl sulfide is used for deposition of CuSCN.

![Figure 4. Scanning Electron Microscopy (SEM) cross-sectional images of FTO/c-TiO2/CH3NH3PbI3/CuSCN assemblies that were fabricated by doctor blading a solution of CuSCN in dipropyl sulfide (a,b) on a chlorobenzene pre-wetted perovskite layer (CBZ→Pr2S) and (c,d) on a dry perovskite layer (Pr2S only). SE: secondary electron images; BS: backscattered electron images. Reproduced with permission from Reference [49]. Elsevier 2017.](image)

Doctor blading is a simple, solution-based and low-cost thin film deposition method that is suitable for roll-to-roll (R2R) device fabrication. It is one of the common deposition methods used for depositing CuSCN HTMs. However, Yang et al. [42] reported that damage of the perovskite layer induced by doctor blading of CuSCN HTM in planar (n-i-p) PSC devices may be the reason for low
performance of planar (n-i-p) devices as compared to inverted (p-i-n) devices. Yang and associates reported an economical simple spray deposition method employing a homemade spray equipment. The CuSCN was dissolved in dilute dipropyl sulfide. The deposition process involved spraying CuSCN at a distance of about 6 cm for 2 s and drying at 80 °C for 5 s. The thickness of the HTM layer was controlled by the number of deposition cycles. Spray deposition resulted in the formation of a uniform CuSCN layer with a thickness of about 50 nm. There was no significant damage to the perovskite layer which was attributed to the minimum contact of the perovskite layer to the dipropyl sulfide solvent. A PCE of 17% was reported for a Au/CuSCN/perovskite/TiO₂/FTO device and a VOC of about 1 V which is typical of organic HTM-based PSCs without additives. Spray coating is a simple deposition method which is compatible with large-scale fabrication. However, Madhavan et al. [44] proved CuSCN deposited by doctor blading can still attain high PCEs in mesoscopic (n-i-p)-based PSC devices. In their work, they reported a PCE of 16.6% for a doctor-bladed CuSCN-based PSC while the spin-coated CuSCN-based device had a 15.4%. The difference in PCE was attributed to different HTM film thickness, with the doctor bladed CuSCN-based film having a thickness of about 500 nm while the spin-coated CuSCN-based had a thickness of about 30 nm as shown in Figure 5. The spin-coated CuSCN thin films were uniform and managed to effectively extract holes even though the films were limited to only 30 nm. When compared to doctor blading, spin coating is not cost effective and is not compatible with a large-scale manufacture where high-throughput fabrication is required. The non-cost effectiveness of spin coating can be attributed to the requirement of large volumes of solvents and raw materials used in spinning coating [50].

Another method which has been used for deposition of CuSCN HTM in PSCs is electrodeposition. Electrodeposition is a simple method which is low cost and is compatible with large-scale fabrication [51]. Shlenskaya et al. [52] reported an electrodeposited CuSCN blocking layer from a solution of CuSO₄, Na₂EDTA, and NaSCN in a three-electrode cell. The electrodeposition mechanism proceeded via nucleation and growth of the resulting CuSCN thin films. Formation of a porous CuSCN involved spin coating the sacrificial polystyrene template on b-CuSCN/ITO substrates from a water/ethanol suspension in the presence of a surfactant. This was followed by electrodeposition of CuSCN into the template at −0.1 V and with the thickness of the deposited film dependent on the potentiostatic deposition time. They obtained a CuSCN film thickness which ranged from 400 to 1400 nm for 0.5–3 layers of CuSCN. Porous CuSCN can be applied in mesoscopic (p-i-n) PSC devices. Nevertheless, Shlenskaya and associates did not report on the optical, stability properties as well as the

**Figure 5.** (a) SEM cross-section of spiro-OMeTAD-based HTM; (b) SEM cross-section of HTM deposited by doctor-blade technique; (c) SEM cross-section of HTM deposited by spin-coating technique; (d) SEM cross-section of PSC without HTM. Reproduced with permission from Reference [44]. American Chemical Society 2016.
photovoltaic performance of porous CuSCN HTM-based PSCs. Hence, there is a need to conduct more research to evaluate the optical stability properties and photovoltaic performance of electrodeposited porous CuSCN-based PSC.

As we have mentioned earlier, finding an ideal solvent for deposition CuSCN HTMs has been a challenge. Research efforts have been dedicated to finding an ideal solvent which can dissolve CuSCN without damaging the perovskite layer. Recently, Murugadoss et al. [53] investigated the suitability of various solvent mixtures in dissolving CuSCN prior to deposition. The solvents were mixed in the following ratios; dipropyl sulfide and chlorobenzene (1:1); isopropanol and methylammonium iodide (MAI) (10 mg/mL); dipropyl sulfide, isopropanol and MAI ((1:2) +10 mg/mL) which were assigned S2, S3 and S4, respectively. The pristine dipropyl sulfide solvent was assigned S1. The photovoltaic parameters of the PSCs fabricated with different solvent ratios are shown here in Table 1.

| Solvent Mixture                                | Sample Codes | JSC (mAcm⁻²) | VOC (V) | FF (%) | PCE (%) |
|------------------------------------------------|--------------|--------------|---------|--------|---------|
| pristine dipropyl sulfide                       | S1           | 18.76        | 0.92    | 56.0   | 9.79    |
| dipropyl sulfide and chlorobenzene (1:1)        | S2           | 18.93        | 0.95    | 49.0   | 8.97    |
| isopropanol and methylammonium iodide (MAI) (10 mg/mL) | S3           | 18.31        | 0.84    | 55.0   | 8.53    |
| isopropanol and MAI ((1:2) +10 mg/mL)           | S4           | 19.42        | 0.92    | 56.0   | 10.07   |

FF = Fill factor.

Murugadoss et al. [53] found that the XRD peak due to PbI² was of low intensity for S1 and higher for other solvents, as illustrated in Figure 6. Figure 6 shows PbI² peaks of higher intensities for S2 and S3. This signified the high dissolution/decomposition rates of the perovskite structure in the presence of other solvents. Hence, the resulting efficiency of the fabricated PSCs was lower as shown in Table 1. Table 2 gives a summary of different solvents, methods and fabrication conditions used in the fabrication of CuSCN thin films.

![Figure 6](image_url). XRD patterns of FTO/bl-TiO₂/m-TiO₂/CH₃NH₃PbI₃/CuSCN film, CuSCN was prepared using different solvents, S1, S2, S3 and S4, deposited by doctor blading method under 80 °C at air atmosphere. The peaks corresponding PbI² and MAPbI₃ are labelled by asterisk the (*) and (◊), respectively. Reproduced with permission from Reference [53]. Elsevier 2017.
Table 2. Fabrication of CuSCN films using different starting material and solvents.

| Starting Material | Solvent Used | Duration | Temp | Additives | Deposition | Thickness (nm) | Ref. |
|------------------|--------------|----------|------|-----------|------------|----------------|-----|
| CuSO₄, KSCN      | DI water     |          | RT   | EDTA      | Electrochemical | 70–90          | [54]|
| CuSO₄, KSCN      | DI water     |          | RT   | DEA       | Electrochemical |                | [55]|
| CuSO₄, KSCN      | DI water     |          | RT   | TEA, EDTA, CDTA, NTA | Electrochemical | 80          | [56]|
| CuSCN            | Dipropyl sulfide | 4 h | RT | | Spin-coating | 300 | [57]|
| CuSCN            | Dipropyl sulfide | Overnight | RT | | Doctor-blading | ~400 | [58]|
| CuSCN            | Dipropyl sulfide | 5 h | RT | | Spin-coating | ~13 | [59]|
| CuSCN            | Dipropyl sulfide | Overnight | RT | | Spin-coating | ~30 | [44]|
| CuSCN            | DMSO         | 2 h      | RT | | Spin-coating |                | [47]|
| CuSCN            | Dipropyl sulfide; Dipropyl sulfide + Chlorobenzene; Isopropanol + MAI | Overnight | RT | | Doctor-blading | 450 | [53]|
| CuSCN            | Diethyl sulfide | 1 h | 50 °C | Ammonia | Spin-coating | 10–40 | [60]|
| CuSCN            | Diethyl sulfide | 1 h | RT | | Spin-coating | 3–5 | [61]|

RT = room temperature; Temp = temperature; DI = deionized DMSO = dimethyl sulfoxide.

4. Architectures Used for CuSCN-Based PSCs

Device structure also plays an important role in the stability and efficiency of PSCs. The mesoscopic device architecture commonly demonstrates higher PCE as compared to planar device architecture. This can be attributed to the greater contact area with perovskite as well as decreased carrier transport distance in mesoscopic PSCs [62]. Having dipropyl sulfide as the solvent of choice during deposition of CuSCN limits the PSC device architecture which can be used. This results in inverted device architecture being the device structure of choice when it comes to CuSCN-based PSCs. However, to the best of our knowledge, there are no reports on mesoscopic (p-i-n) CuSCN-based PSCs. CuSCN films were first fabricated on the mesoporous structure by Ito et al. [63] and the structure proposed was FTO/compact TiO₂/mesoporous TiO₂/CH₃NH₃PbI₃₋ₓClₓ/CuSCN/Au which achieved a low PCE of 4.85%. Even though mesoscopic structure-based PSCs with spiro-OMeTAD HTM have exhibited high efficiency of 22.1%, they require high temperature during fabrication of mesoporous TiO₂ layer which is not good for flexible PSCs [64] and does not bode well with characteristics of an ideal HTM. Hence, regular and inverted planar architectures were taken into consideration.

The first inverted planar architecture dates back to 2013; it was reported by Chen et al. [27] where it was applied in PSCs using PEDOT:PSS as the HTM. Unfortunately, their device degraded abruptly due to the acidic and hygroscopic nature of PEDOT:PSS. The inverted planar architecture was also introduced in inorganic HTM-based PSCs and has shown promising results as it requires low-temperature processing conditions. This makes it compatible with flexible substrates and moreover, inverted planar devices exhibit high FF [65,66]. Inverted planar architecture offers an easy device structure which is compatible with large-scale fabrication. Furthermore, it has comparable conversion efficiency with a mesoporous device structure, and negligible hysteresis effect made this structure the best so far [57,58]. The regular planar-based CuSCN PSCs, on the one hand, have exhibited high conversion efficiency and stability. Additionally, the planar structure is characterized by low-temperature processing requirements, low-cost, tunable device performance and an architecture that is capable of employing different interfacial materials [67,68]. In the following sub-sections, we discuss some of the regular planar and inverted planar-based CuSCN films structures and their device performances that have been reported to date.

4.1. n-i-p Architecture of CuSCN-Based PSCs

In 2014, Chavhan et al. [69] worked on organo-metal halide PSCs with CuSCN as the inorganic hole selective content and glass/FTO/TiO₂/CH₃NH₃PbI₃₋ₓClₓ/CuSCN/Au as the device architecture. The fabricated planar PSCs were annealed at different temperatures; thereafter, solar cell characterization was performed. In their work, they discovered that PSC device annealed at 110 °C showed improved performance with a PCE of 6.4%. The photovoltaic performance parameters
of other PSCs with planar structure glass/FTO/TiO₂/CH₃NH₃PbI₃₋ₓClₓ/CuSCN/Au annealed at different temperatures are shown here in Table 3.

| Annealing Temp. (°C) | Jsc (mAcm⁻²) | Voc (V) | FF (%) | PCE (%) |
|---------------------|--------------|---------|--------|---------|
| 90                  | 13.04        | 0.49    | 49.0   | 3.1     |
| 100                 | 14.27        | 0.67    | 48.1   | 4.5     |
| 110                 | 14.4         | 0.73    | 61.7   | 6.4     |
| 120                 | 11.1         | 0.45    | 53.8   | 2.7     |

Temp. = temperature.

It is clearly evident from Table 3 and Figure 7 that annealing had a great impact on solar cell performance as it has exhibited different photovoltaic performances at different annealing temperatures. It is also evident from Table 3 that the planar PSC structure yielded impressive results and even achieving a good FF of 61.7% which signifies good carrier selectivity. The efficiency of the CuSCN-based PSC was comparable to the first spiro-OMeTAD-based PSC with an efficiency of 9.7% [8]. However, the Voc of the planar PSC structures was a major setback, with a reported low value of 0.45 V which is indicative of short diffusion length of <0.75 V for CuSCN. The low Voc was attributed to high recombination rates originating from both perovskite material and CuSCN inorganic HTM. It is highly recommended to ensure that the charge carrier extraction in selective contacts is well-balanced in order to enhance the performance of planar heterojunction PSC device to reach high photocurrents.

Arora et al. [70] reported a CuSCN-based PSC which exhibited high efficiency of 20.3% and this was attributed to reduced contact time between the perovskite layer and solvent during HTM deposition. The reduced interaction between the perovskite material and the solvent used for dissolution of CuSCN was made possible by using a dynamic deposition approach whereby, the solvent is evaporated rapidly as compared to the conventional deposition approach. They reported that the rapid evaporation of solvent induced nucleation and growth of CuSCN nanostructures and high density of nucleation formed compact and thin CuSCN films with nano-crystallites. This deposition approach has potential to improve the stability, as well as the photovoltaic performance of inorganic HTM-based PSCs since perovskite dissolution in solvents used in HTM deposition has been one of their major drawbacks.

Arora and associates also gave an insight on issues of instability in CuSCN-based PSCs. In their work, they introduced a thin spacer layer of reduced graphene oxide (rGO) using spin coating before depositing the Au layer with a resulting overall structure: FTO/compact TiO₂/mesoporous...
Arora et al. [70], CuSCN-based PSC with carbon electrode lags far behind in terms of efficiency. Xiong et al. [46] reported an inverted PSC which employed CuSCN modified PEDOT:PSS as HTM. Table 4 presents the respective photovoltaic performance parameters. Device B was found to degrade during the light soaking test. In previous reports, it was reported that the solvent used for dissolving the CuSCN but rather the oxidation of the gold cathode when the CuSCN-based device is undergoing the light soaking test. In previous reports, it was reported that the solvent used in deposition of CuSCN layer tend to dissolve the perovskite material but the X-ray photoelectron spectroscopy (XPS) reported by Arora and co-workers proved the results otherwise. The approach of introducing a thin spacer layer improved the carrier extraction and collection processes which resulted in a PCE of 20.4% with Jsc of 23.40 mA cm⁻², Voc of 1.10 V and FF of 77.2%. Baranwal et al. [71] replaced the Au electrode with a low temperature-processed carbon electrode in a mesoscopic CuSCN-based PSC for the first time. CuSCN reduces the difference in energy between the valence band of the CH₃NH₃PbI₃ perovskite and the Fermi level of the carbon electrode which allows smooth path for transport of holes. The use of CuSCN resulted in reduced recombination losses and this led to a moderate efficiency of 12.4%. However, when compared to CuSCN-based PSC reported by Arora et al. [70], CuSCN-based PSC with carbon electrode lags far behind in terms of efficiency.

4.2. Inverted (p-i-n) Architecture of CuSCN-Based PSCs

In 2015, Ye et al. [72] reported on CuSCN-based inverted planar perovskite solar cell. Deposition of CuSCN was carried via a one-step deposition for device A, while two-step sequential deposition process was used for device B. Figure 9 shows the SEM cross-sectional images of the two devices and Table 4 presents the respective photovoltaic performance parameters. Device B was found to degrade rapidly due to percolation of air and moisture to the perovskite layer.

Table 4. The photovoltaic performance of Device A and B deposited using different techniques.

| Device | Jsc (mA cm⁻²) | Voc (V) | FF (%) | PCE (%) |
|--------|---------------|---------|--------|---------|
| Device A | 21.9          | 1.00    | 75.8   | 16.6    |
| Device B | 21.4          | 0.92    | 68.1   | 13.4    |

One of the inherent advantages of organic-based HTMs is their low-temperature processability. This has been a challenge in inorganic HTMs as they require high temperatures for deposition. Recently, Xiong et al. [46] reported an inverted PSC which employed CuSCN modified PEDOT:PSS as HTM.
resulting in an HTM bilayer. Their approach was similar to that reported by Hu et al. [73], where PEDOT:PSS and CuI were used as bilayer HTM which resulted in improved stability and efficiency. Xiong et al. [46] reported a PCE of 10.09%, which was relatively higher than of the PEDOT:PSS-based PSC control (9.1%). The CuSCN modified PEDOT:PSS-based device exhibited improved Voc and this could be attributed to a better-matched energy alignment between MAPbI₃ and CuSCN modified PEDOT:PSS HTM. The PEDOT:PSS and CuSCN were spin-coated and annealed at 120 °C and 60 °C respectively. When compared to annealing temperatures mentioned in Table 3, the CuSCN modified PEDOT:PSS-based performed better at relatively similar annealing temperatures. Wang et al. [74] also reported improved photovoltaic performance for a CuSCN/CuI composite-based PSC. The CuSCN/CuI composite-based PSC had an efficiency of 18.76% as compared to 14.53% and 16.66% for CuI-based PSC and CuSCN-based PSC respectively. Presence of CuSCN resulted in formation of good quality HTM thin films which resulted in improved efficiency. Modification of CuSCN HTM might be one avenue that can be explored in order to have improved HTMs which meet properties of ideal HTMs, as well as being cost-effective. Table 5 shows the summary of some CuSCN-based PSCs and their photovoltaic performances.

| Device Architecture | Device Jsc (mA/cm²) | Voc (V) | FF (%) | PCE (%) | Year | Reference |
|---------------------|---------------------|---------|--------|---------|------|-----------|
| FTO/compact TiO₂/mesoporous TiO₂/CsFAM | 23.39 | 1.10 | 76.1 | 20.39 | 2017 | [70] |

Table 5 shows the CuSCN HTM-based PSCs with their different device gestalts, the photovoltaic performances and the year of publication. The device with the lowest efficiency is 4.85% and was reported in 2014 and the device with the highest efficiency was reported in 2018 with an efficiency of 20.39%. This shows the conversion efficiency of CuSCN HTM has rapidly improved in the past 5 years using different synthesis methods and device architectures. Additionally, Table 6 presents the comparative PSC device performance employing different HTMs.

It is clearly evident from Table 6 that PSCs employing PTAA and spiro-OMeTAD HTMs have achieved the maximum PCE of 22.1% and 21.6%, respectively, whilst the PSC employing CuSCN HTM has achieved a noble efficiency of 20.4% in a mesoscopic device architecture which is the most promising of the fabricated CuSCN HTM. Though the efficiency of PSC employing inorganic HTM such as CuSCN is still lower as compared to the spiro-OMeTAD and PTAA HTM, inorganic HTMs are more economical. Spiro-OMeTAD and PTAA require additives, moreover these HTMs are not compatible with large-scale manufacturing processes. Yet the preparation of PSC employing inorganic HTMs is far much economical and is more feasible for solar panel industry. It would be ideal to fabricate PSC consisting of HTM bilayers or composite HTMs such as CuSCN/CuI and CuSCN/NiO.
without encapsulation. The PCE was reduced by 5.8% only when the CuSCN-based PSC was exposed
well as the perovskite layer when exposed to moisture. The morphology of spiro-OMeTAD is also
The KSCN post-treated CuSCN PSC managed to retain about 90% of its initial PCE after 50 days in
untreated CuSCN-based PSC.

This is evident from the reported 14.90% PCE for KSCN post-treated CuSCN-based PSC as
compared to 11.90% for untreated CuSCN-based PSC. This is evident by the reduction of PCE from 16.46% to 14.32% for CuSCN-based PSC while the
thermal stability, the CuSCN-based PSC also fared much better than the spiro-OMeTAD-based control
PSC which reduced by 30%, it is clear that the CuSCN-based performed exceptionally well. In terms of
thermal stability, the KSCN post-treated CuSCN-based PSC. This is evident by the reduction of PCE from 16.46% to 14.32% for CuSCN-based PSC while the
CuSCN used as HTM in spiro-OMeTAD results in reduced stability of
PSCs as well. Recently, Yang et al. [42] reported a remarkable stability of a CuSCN-based PSC
commercialization. Besides perovskite materials, HTMs are also known to contribute to the long-term
stability of PSCs. For example, the use of additives in spiro-OMeTAD results in reduced stability of
PSCs due to presence of excess SCN⁻ from the KSCN, since excess SCN⁻ increase the hole conductivity
of CuSCN. This is evident from the reported 14.90% PCE for KSCN post-treated CuSCN-based PSC as
compared to 11.90% for untreated CuSCN-based PSC.

5. Stability of CuSCN-Based PSCs

Stability issue is one of the major drawbacks that limit the perovskite-based solar cells from
commercialization. Besides perovskite materials, HTMs are also known to contribute to the long-term
stability of PSCs. For example, the use of additives in spiro-OMeTAD results in reduced stability of
PSCs. This is due to the hygroscopic nature of the additives which leads to degradation of the HTM as
well as the perovskite layer when exposed to moisture. The morphology of spiro-OMeTAD is also
a cause of concern as it has pin-holes which are a source of degradation in PSCs [50,81]. PEDOT:PSS is
the choice HTM for inverted (p-i-n) PSC devices. However, it is a source of instability in PSCs as it is
hygroscopic and acidic in nature [82,83]. Thermal stability is also of paramount importance in HTMs
since solar panels are exposed to very high temperatures when operating. Therefore, solar panels must
be able to withstand a temperature of up to 85 °C according to international standards [84].

Introduction of inorganic HTMs has not only been a move to lower cost of PSCs but as a way to improve the stability of PSCs as well. Recently, Yang et al. [42] reported a remarkable stability of a CuSCN-based PSC
without encapsulation. The PCE was reduced by 5.8% only when the CuSCN-based PSC was exposed to
30% relative humidity for 100 days indoors. When compared to the spiro-OMeTAD-based control
PSC which reduced by 30%, it is clear that the CuSCN-based performed exceptionally well. In terms of
thermal stability, the CuSCN-based PSC also fared much better than the spiro-OMeTAD-based control
PSC. This is evident by the reduction of PCE from 16.46% to 14.32% for CuSCN-based PSC while the
spiro-OMeTAD reduced to as low as 5.29% from 17.63% after encapsulation at 120 °C for 5 min.

Lyu et al. [76] reported better stability of KSCN post-treated CuSCN-based inverted planar PSC. The KSCN post-treated CuSCN PSC managed to retain about 90% of its initial PCE after 50 days in ambient humid conditions in the dark as compared to 60% for untreated CuSCN-based PSC as shown in Figure 10 a. The encapsulated KSCN post-treated CuSCN-based PSC also fared better than the untreated CuSCN-based PSC when exposed to continuous illumination under one sun as shown in Figure 10 b. The relative better stability of the KSCN post-treated CuSCN-based PSC was attributed to reduced trapped charges at the perovskite/CuSCN interface. Post-treating CuSCN film with KSCN did not only improve stability, it also improved photovoltaic performance of the cell. This might have been due to presence of excess SCN⁻ from the KSCN, since excess SCN⁻ increase the hole conductivity of CuSCN. This is evident from the reported 14.90% PCE for KSCN post-treated CuSCN-based PSC as compared to 11.90% for untreated CuSCN-based PSC.

Table 5. Summary of photovoltaic device performance of CuSCN HTMs for PSCs.

| Device Architecture | Device Type | Jsc (mA/cm²) | Voc (V) | FF (%) | PCE (%) | Year | Reference |
|---------------------|-------------|-------------|--------|--------|---------|------|-----------|
| FTO/compact TiO₂/mesoporous TiO₂:FAPbI₃:CH₃NH₃PbI₃/CuSCN/Al | M | 23.39 | 1.10 | 76.1 | 20.39 | 2017 | [70] |
| FTO/blocking TiO₂/mesoporous TiO₂:FAPbI₃:CH₃NH₃PbI₃/CuSCN/Al | M | 23.1 | 1.04 | 75.3 | 18.0 | 2016 | [75] |
| FTO/compact TiO₂/mesoporous TiO₂:FAPbI₃:CH₃NH₃PbI₃/CuSCN/Al | M | 23.10 | 1.01 | 73.1 | 17.10 | 2017 | [42] |
| FTO/CuSCN/MAPbI₃−ₓClₓ/Pc₆BM/Pe@/Ag | IP | 20.76 | 1.10 | 73.0 | 16.66 | 2018 | [74] |
| FTO/CuSCN/CuI/MAPbI₃−ₓClₓ/Pc₆BM/Pe@/Ag | IP | 22.33 | 1.11 | 76.0 | 18.76 | 2018 | [74] |
| FTO/blocking TiO₂/mesoporous TiO₂:FAPbI₃:CH₃NH₃PbI₃/CuSCN/Al | M | 21.80 | 1.10 | 69.2 | 16.6 | 2016 | [44] |
| FTO/CuSCN/CuI/MAPbI₃−ₓClₓ/C60/PCBM/Ag | IP | 21.9 | 1.00 | 75.8 | 15.6 | 2015 | [72] |
| FTO/CuSCN/CuI/MAPbI₃−ₓClₓ/PCBM/BCP/Ag | IP | 19.20 | 1.01 | 77.0 | 14.90 | 2019 | [76] |
| FTO/CuSCN/CuI/MAPbI₃−ₓClₓ/PCBM/BCP/Ag | IP | 18.21 | 1.03 | 76.1 | 14.28 | 2016 | [60] |
| FTO/dense-TiO₂/mesoporous TiO₂:FAPbI₃:CH₃NH₃PbI₃/CuSCN/Carbon | M | 18.90 | 0.96 | 68.0 | 12.41 | 2018 | [71] |
| FTO/CuSCN/ PEDOT:PSS/CH₃NH₃PbI₃/Ag | IP | 17.76 | 1.06 | 62.2 | 10.8 | 2015 | [59] |
| FTO/CuSCN/ PEDOT:PSS/CH₃NH₃PbI₃/Ag | IP | 17.6 | 0.86 | 71.7 | 10.99 | 2018 | [46] |
| FTO/blocking TiO₂/mesoporous TiO₂:FAPbI₃:CH₃NH₃PbI₃/CuSCN/Al | M | 16.82 | 0.89 | 61.4 | 9.20 | 2018 | [58] |
| FTO/blocking TiO₂/mesoporous TiO₂:FAPbI₃:CH₃NH₃PbI₃/CuSCN | M | 19.15 | 0.93 | 56.0 | 10.04 | 2017 | [53] |
| FTO/compact TiO₂:CuSCN/Al | P | 19.3 | 0.84 | 59.6 | 9.6 | 2017 | [49] |
| FTO/CuSCN/Al | P | 18.53 | 0.73 | 61.7 | 6.4 | 2014 | [69] |
| FTO/dense-TiO₂/mesoporous TiO₂:FAPbI₃:CH₃NH₃PbI₃/CuSCN | M | 23.39 | 1.10 | 76.1 | 20.39 | 2017 | [70] |

M = Mesoscopic (n-i-p) device; P = Planar (n-i-p) device; IP = Inverted planar (p-i-n) device.
Table 6. Comparison of efficiency of CuSCN-based PSC with other HTMs.

| HTM          | Jsc (mAcm$^{-2}$) | Voc (V)  | FF (%) | PCE (%) | Reference |
|--------------|-------------------|----------|--------|---------|-----------|
| CuSCN        | 23.39             | 1.1      | 76.1   | 20.4    | [70]      |
| Spiro-OMeTAD | 24.57             | 1.11     | 79.2   | 21.6    | [2]       |
| PTAA         | 24.1              | 1.1      | 81.90  | 22.1    | [77]      |
| NiO          | 20.2              | 1.06     | 81.3   | 17.3    | [78]      |
| CuI          | 22.8              | 1.01     | 73     | 16.8    | [20]      |
| CuPc         | 23.19             | 1.13     | 73.1   | 18.68   | [79]      |
| Li$_{0.05}$Mg$_{0.15}$Ni$_{0.8}$O | 22.68          | 1.12     | 77     | 19.58   | [80]      |

Jung et al. [75] tested the intrinsic thermal stability of CuSCN and spiro-OMeTAD materials using thermogravimetric analysis (TGA). There was relatively no observed weight loss for both samples exposed to air or nitrogen at 125 °C for 2 hours as shown in Figure 11. They went on to investigate the thermal stability of CuSCN-based PSC at 125 °C for 120 minutes in air at 40% relative humidity in the dark. The CuSCN-based PSC managed to retain more than 60% of its initial efficiency while the spiro-OMeTAD-based control PSC had a dramatic efficiency reduction from 18.4% to 4.6%.

Figure 10. Time-dependent PCE of PSCs depending on post-treatment with KSCN at different condition of (a) ambient atmosphere with low humidity (the devices kept in the vacuum chamber in the dark before and after measurements), (b) relative humidity (RH) of 70% and (c) continuous illumination under one sun (the devices were encapsulated). Reproduced with permission from Reference [76]. Elsevier 2019.

Figure 11. TGA curves of pristine FAPbI$_3$ (black) and CuSCN (red) powders at 125 °C in air for 2 h, equivalent to the thermal stability testing conditions. Reproduced with permission from Reference [75]. Wiley 2016.
This goes to show that when it comes to thermal stability, CuSCN HTM performs much better than spiro-OMeTAD. Recently, Chowdhury et al. [60] reported a modified CuSCN/rGO bilayer-based PSC. The rGO/CuSCN-based PSC exhibited better stability under light soaking test for 100 h. It had an efficiency reduction of about 10% as compared to the pristine CuSCN-based PSC which had about 50% efficiency reduction under the same conditions. Modification of HTMs might result in materials with improved properties. In general, CuSCN-based PSCs exhibit better stability as compared to organic-based PSCs. However, there is a need to test the stability of PSCs under the standard thermal test conditions rather than doing it under shorter periods of times. It would also result in clear comparisons among tested solar cells.

6. Recommendations and Conclusions

Perovskite solar cells have shown promising characteristics as an alternative to expensive silicon solar technology with the high efficiency of 25.6%. However, the drawbacks caused by sensitivity of organic–inorganic halide-based PSCs to UV radiation and moisture make these solar cells inapplicable for large-scale practical applications. Research on developing inexpensive and stable materials for hole transport materials, such as inorganic semiconductors to replace organic HTMs like spiro-OMeTAD, has been the main priority. Research and development of inorganic HTMs have received significant attention due to the fact that inorganic HTMs are more stable, affordable, have high hole mobility, wide band gap, high transparency, high chemical stability, can be deposited at low temperatures and have simple synthetic routes which can be tailored to industrial scale. In lieu of these observations, this review paper has provided the current progress on the development of PSCs employing inorganic HTM. More specifically, the current progress on PSC employing CuSCN HTM has been provided in detail. This review paper has shown that CuSCN HTM thin films can be deposited by simple and affordable techniques. In this review, we have shown that CuSCN HTM thin films have been deposited by doctor blading, spin coating, spray deposition, and even electrodeposition. Our review has shown that the highest PSC PCE was achieved with a device that had thin films deposited by spray deposition (17.10%), followed by doctor blading (16.6%) and spin coating (15.6%). We also, discovered that the nature of the solvent used in the deposition of these thin films had an impact on the photovoltaic performance of the PSC. To that end, various solvents have been reported to try to reduce the dissolution rates of the perovskite material. Various solvents like dipropyl sulfide, chlorobenzene, isopropanol, methylammonium iodide (MAI), DMSO, and deionized water have been explored to date. Additionally, various solvent mixtures have also been explored with the highest PCE in PSC being reported for PSC with of 10.07% achieved with isopropanol and MAI. However, the search for an ideal solvent to deposit CuSCN thin films is still on. In this review, we have also, shown that device architectures in PSCs employing CuSCN as HTM also play a crucial role in the photovoltaic performance of the PSC. Our review has shown that the mesoscopic device architecture commonly employed for PSCs with spiro-OMeTAD which has a PCE of 21.1% whilst the PSC employing CuSCN as HTM has a reported PCE of 4.85% and a high PCE of 20.3% was reported for n-i-p architecture. We also reported planar and inverted planar device architectures employing CuSCN as HTM; the highest conversion efficiency reported for planar device architecture is 9.6%, whilst that of an inverted planar device is 15.6%. This shows that mesoporous device architecture is by far the best architecture to use for CuSCN-based PSCs as all the top five devices reported with the highest efficiency are of the mesoscopic devices.

It has been reported that inorganic HTMs are more thermally stable when exposed to weather elements as compared to organic HTMs such as spiro-OMeTAD and PEDOT:PSS. CuSCN being an inorganic HTM is no exception. In this review, CuSCN has shown remarkable stability when exposed to weather elements. However, it is difficult to give a comparative analysis of the stability of CuSCN-based PSCs, and this is due to the reported stability tests being carried out at different test conditions. Perhaps carrying out stability tests under standard test conditions might give a more accurate comparison. This paper has provided a detailed review of the progress achieved to date on
the use of CuSCN as HTM in PSCs. The triumphs and challenges of the PSC employing CuSCN as HTM has been discussed here in detail.

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