A brief review of hole transporting materials commonly used in perovskite solar cells

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Abstract Perovskite solar cells (PSCs) have been brought into sharp focus in the photovoltaic field due to their excellent performance in recent years. The power conversion efficiency (PCE) has reached to be 25.2% in state-of-the-art PSCs due to the outstanding intrinsic properties of perovskite materials as well as progressive optimization of each functional layer, especially the active layer and hole transporting layer (HTL). In this review, we mainly discuss various hole transporting materials (HTMs) consisting of HTL in PSCs. The progress in PSCs is firstly introduced, then the roles of HTL playing in photovoltaic performance improvement of PSCs are emphasized. Finally, we generally categorize HTMs into organic and inorganic groups and demonstrate both their advantages and disadvantages. Specially, we introduce several typical organic HTMs such as P3HT, PTTA, PEDOT:PSS, spiro-OMeTAD, and inorganic HTMs such as copper-based materials (CuO_x , CuSCN , CuI , etc.), nickel-based materials (NiO_x), and two-dimensional layered materials (MoS_2 , WS_2 , etc.). On basis of reviewing the reported HTMs in recent years, we expect to provide some enlightenment for design and application of novel HTMs that can be used to further promote PSCs performance.

Keywords Perovskite solar cells; Hole-transporting materials; Power conversion efficiency

1 Introduction

In recent decades, the energy consumption has greatly risen with the rapid development of social economy. Therefore, it has been in urgent need of exploring renewable, sustainable, efficient, and clean energy sources to take the place of traditional fossil fuels. Solar energy is one of the most suitable alternatives that is almost inexhaustible and of huge strong radiation. How to efficiently use it so as to improve the power conversion efficiency (PCE) has attracted tremendous attentions [1–4].

Perovskite solar cells (PSCs) are a novel type of photovoltaic systems. It has experienced a rapid development since its advent in 2009 and the state-of-the-art verified PCE has been as high as 25.2%, making it comparable to traditional silicon-based solar cells. Due to the inherent features of perovskite materials, PSCs shows excellent photovoltaic performance, while it also owes to a progressive optimization of materials consisting of each functional layers, processing, and device structure [5]. Specially, it is found that the suitable perovskite material and/or charge transporting materials are indispensable to the achievement of high-performing PSCs. Lead-halide perovskites have been considered to be the most widely used light absorbing materials while a large number of reports on the hole transporting materials (HTMs) have demonstrated the significant effects of hole transporting layer (HTL) taking in the processes of hole extraction and transportation. Generally, HTL plays particular roles as following: (i) it extracts and transports the holes in the active layer to the electrode; (ii) it acts as an energy barrier to prevent the transfer of electrons to the anode; (iii) it separates the perovskite layer from the anode and isolates the moisture in the air, improving the devices stability by

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reducing possible degradation and corrosion; (iv) it can help to improve the open circuit voltage (V_{oc}) when its highest occupied molecular orbital (HOMO) energy level is well matched [6, 7].

In this article, we mainly review the reported HTMs of PSCs in recent years. This article includes a general introduction of PSCs, the performance of various HTMs in PSCs and their advantages as well as the deficiencies in detail.

1.1 Perovskite solar cells (PSCs)

PSCs were originally grown by replacing the organic molecular dyes with perovskite materials in liquid-type dye-sensitized solar cells (DSSCs) and the first report on it was made by Miyasaka and co-workers in 2009 [8]. They adopted organometal halide perovskite as light absorber to fabricate the first perovskite device, obtaining an exciting PCE value of 3.8%. Perovskite materials usually exhibit intriguing features of high absorption coefficient, long diffusion length, tunable bandgap, low carrier recombination loss and high carrier mobility, making it a promising candidate to advance photovoltaic technology. It can be illustrated in a formula of ABX_3 [$A = FA^+$ ($NH_2CH = NH_2^+$), MA^+ ($CH_3NH_3^+$); $B = Pb^{2+}$; $X = Cl^-$, Br^- , or I^-] [9] and its crystal structure is shown in Fig. 1. In each unit cell, there are 6 halide ions located at the center of cube face. Connecting these 6 halide ions can make an octahedron. Each octahedron shares one of its halogens with neighboring octahedrons, resulting in the unique structure of perovskites. Additionally, such structure can accommodate a variety of elements that greatly enrich perovskite family. However, these perovskite materials especially organometal halide perovskites are inevitably dissoluble in the liquid redox electrolyte of DSSCs, which induces the photovoltaic performance degrading rapidly. Therefore, people tried to utilize solid-state HTMs to take the place of liquid electrolyte and PSCs structurally evolved, as shown

Fig. 1 Three-dimensional crystal structure of perovskite. Reproduced with permission from Ref. [8]. Copyright 2009 American Chemical Society

in Fig. 2 [10]. Park and co-workers reported a lead iodide perovskite sensitized all-solid-state mesoscopic PSCs in 2012 [11]. They chose organic 2,2',7,7'-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMe-TAD) as HTM to replace the liquid electrolyte, obtaining high efficiency up to 9.7% and 500 h long-term stability without device encapsulation. They also demonstrated that the achievement of good performance only needed a thin mesoporous TiO_2 layer in submicron scale. Soon afterward, Snaith and co-workers reported a meso-superstructured PSCs with mesoporous Al_2O_3 as an inert scaffold, improving the PCE to 10.9% [12]. More importantly, they confirmed that PSCs could work without the typical mesoporous TiO_2 layer, suggesting that electrons could transfer through in the perovskite layer. Meanwhile considerable efforts were also made to explore methods by that PSCs could be fabricated at a low temperature without high temperature sintering of TiO_2 or Al_2O_3 mesoporous scaffold. In 2013, Snaith's group introduced the meso-superstructure into thin-film solar cells to get a low-temperature processed PSCs with a PCE of 12.3% [13, 14]. They further removed the mesoporous scaffold to study its effect on device performance, promoting the generation of planar PSCs. Several months later, a simple planar heterojunction PSCs without mesoporous scaffold was successfully fabricated and achieved a high efficiency up to 15% [15]. Since then, planar PSCs have been widely developed, and the state-of-the-art PCE has been reported over 23%.

1.2 Structure of PSCs

PSCs are structurally divided into two categories: planar and mesoporous structure [16, 17]. Mesoporous structure was used to be dominant as PSCs is originated from DSSCs. For mesoporous PSCs, a scaffold is required as shown in Fig. 3. The scaffold materials can be conductive TiO_2 and ZnO (Fig. 3a), also can be insulating Al_2O_3 and ZrO_2 (Fig. 3b). For planar PSCs, it is relatively easy to fabricate due to the unique characteristics of solution processing of perovskite films. Planar PSCs typically consist of layered perovskite located in the middle and charge transporting layers that are sandwiched between the electrodes (Fig. 3c). They can be implemented in conventional (n-i-p) or inverted (p-i-n) architecture, depending on the location of charge transporting layers [18, 19]. There also have been some reports on PSCs without electron transporting layer (ETL) (Fig. 3d) or HTL (Fig. 3e), which could make scalable manufacturing at low cost and simplifying device architecture realizable. Nevertheless, the highest PCE of these ETL-free or HTL-free PSCs was 20.0% as Wu and co-workers [20, 21] reported in 2018, which is difficult for further advance so far. Therefore,

Fig. 2 Development of perovskite solar cell structure: **a** mesoporous structure in which TiO_2 is used as scaffold, **b** meso-superstructure concept in which Al_2O_3 is used as scaffold, **c** pillared structure with a TiO_2 building block, **d** planar heterojunction structure. Reproduced with permission from Ref. [10]. Copyright 2014 Elsevier Ltd

Fig. 3 Schematic diagram of common perovskite solar cell device structure: **a** mesoporous structure, **b** meso-superstructure, **c** conventional planar structure, **d** electron selective contacts (ESC)-free structure, **e** hole selective contacts (HSC)-free structure, and **f** invert planar structure. Reproduced with permission from Ref. [16]. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

ETL and HTL are still essential to fabricate high-efficiency PSCs.

1.3 Hole transporting materials (HTMs) for PSCs

An ideal HTM candidate possesses an intrinsically high hole mobility, suitable energy levels that match with the perovskite layer, long-term stability in air as well as good photochemical and thermal stability. It should also be solution-processed so as to prepare HTL especially when it is used in the conventional (n-i-p) PSCs. For scalable manufacturing and further commercial application, low cost and easy preparation of HTMs should also be taken into account [7, 22–24].

HTMs were firstly adopted in all solid states PSCs in 2012 as stated above and organic spiro-OMeTAD was employed. So far, spiro-OMeTAD is still the most popular HTM for high-performing PSCs, but it only works effectively in combination with some additives, for example, 4-tert-butylpyridine (tBP) and bis (trifluoromethane) sulfonimide lithium salt (Li-TFSI) [25]. Dopant-free HTMs such as PEDOT:PSS [poly (3,4-ethylenedioxythiophene): polystyrene sulfonate] and P3HT [poly(3-hexylthiophene-2,5-diyl)] have also been developed [26–29]. Our group also reported a dopant-free P1-based PSCs which achieved a PCE of 18.30% [30]. Though these organic HTMs exhibit disadvantages of instability, multi-step synthesis etc., they were utilized in almost all the state-of-the-art PSCs. In comparison, inorganic HTMs are of good stability, high

hole mobility, low cost etc. [31–33]. Till now, inorganic HTMs of Cu_2O , CuO , CuI , CuSCN , NiO_x , and MoS_2 have been intensively studied and showed great performance. In addition, CuS , CuCrO_2 , MoO_x , WO_x have also been reported [24]. The energy level of these HTMs and other commonly used materials in PSCs are shown in Fig. 4. And the particular discussion is as follows.

2 Organic HTMs

Spiro-OMeTAD, PEDOT:PSS, PTAA (poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine]) and P3HT are typical organic HTMs used in PSCs (Fig. 5) and their hole mobilities are shown in Table 1 [25, 34, 35]. Besides, there are also other new organic HTMs reported and some of them are considered to be promising candidates [36–38]. In this section, we will discuss these organic materials and show the performance of PSCs based on them. Detailed photovoltaic parameters are summarized in Table 2 [34, 35, 39–69].

2.1 Spiro-OMeTAD

Spiro-OMeTAD is of high-glass transition temperature (T_g), amorphous nature, and proper energy levels. Among numerous HTMs in the PSCs, it is still dominant. However, the hole mobility (μ_h) of the pristine spiro-OMeTAD was calculated to be only about $2 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ by the

space charge limited current (SCLC) model. This can be improved by more than an order of magnitude with an optimal addition of Li-TFSI and tBP. It was demonstrated that μ_h enhancement could be contributed to the increased disorder and broadened tail of the density of states induced by the presence of Li^+ , while tBP dopants could increase the solubility of Li-TFSI, and therefore, remarkably improve the homogeneity of spiro-OMeTAD film. Moreover, to implement small amount of cobalt- or antimony-based salts, for example, tris (2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) tris-(bis(trifluoromethylsulfonyl)imide)) (FK209) and $\text{N}(\text{PhBr})_3\text{SbCl}_6$ in Li-TFSI and tBP doped spiro-OMeTAD could lead to increased electrical conductivity. Consequently, the PCE of PSCs based on spiro-OMeTAD was greatly promoted by selecting suitable additives. More importantly, the highest PCE of PSCs got improved in combination with continuous optimization of light absorbing materials and processing, making doped spiro-OMeTAD the most widely used HTM in PSCs. In most of cases, spiro-OMeTAD was just doped with Li-TFSI and tBP. In 2014, Jeon et al. [39] synthesized three spiro-OMeTAD derivatives with two methoxy substituents located in different positions in each of the quadrants. These derivatives doping with Li-TFSI and tBP were employed as HTMs in mesoporous PSCs. The devices with o-OMe substituted spiro-OMeTAD performed a much higher PCE up to 16.7% compared to that of the devices with other derivatives. In 2016, Bi et al. [40] showed a mesoporous PSCs based on spiro-OMeTAD and dopants of

Fig. 4 Energy level diagrams of commonly used materials in perovskite solar cells

Fig. 5 Chemical structures of several common organic HTMs: **a** spiro-OMeTAD, **b** PEDOT:PSS, **c** PTAA, **d** P3HT

Table 1 Comparison of hole mobility of several common organic HTMs ($\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$)

Pristine spiro-OMeTAD	Li-TFSI doped spiro-OMeTAD	Pristine PTAA	Li-TFSI/t-BP doped PTAA	Amorphous P3HT	Self-assembled P3HT nanofibrils
2×10^{-4} [25]	2×10^{-3} [25]	7.47×10^{-5} [34]	4.28×10^{-4} [34]	1×10^{-5} [35]	0.1 [35]

Li-TFSI, tBP and FK209. They adopted a new one step method to produce perovskite films from a mixed solution of FAI, PbI_2 , MABr and PbBr_2 . The maximum PCE and open-circuit voltage of the prepared PSCs were 20.8% and 1.18 V, respectively. In 2017, Jiang et al. [41] systematically studied the influence of the PbI_2 contents on photovoltaic performance of spiro-OMeTAD-based devices. It was found that a moderate residual of PbI_2 could provide the devices with stable and high PCE. For conversional (n-i-p) planar PSCs with moderate residual PbI_2 in perovskite layer, PCE of 21.6% and 20.1% was achieved in small size (0.0737 cm^2) and in large size (1 cm^2), respectively. Then in 2019, Jiang et al. [42] adopted an organic halide salt, phenethylammonium iodide (PEAI) to reduce the defects and suppress non-radiative recombination on the perovskite surface. The PEA solution was directly spin-coated onto the $\text{HC}(\text{NH}_2)_2\text{-CH}_3\text{NH}_3$ mixed perovskite layer without any additional process. The planar PSCs with doped spiro-OMeTAD exhibited a certified PCE of 23.32% and a V_{OC} of 1.18 V. As far as we know, it is the highest record of planar PSCs based on spiro-OMeTAD HTMs even though the device thermal stability was not good enough. The structure and photovoltaic performance of the device are shown in Fig. 6.

Besides spiro-OMeTAD could be used as HTM in the typical organic-inorganic hybrid PSCs, it also was

employed in other PSCs with new light absorbing materials or processing. In 2017, Di and co-workers [70] reported a scalable sheet-to-sheet slot die coating process that was developed on $152.4 \text{ mm} \times 152.4 \text{ mm}$ glass/ITO substrates covered with two functional layers: the perovskite layer and the spiro-OMeTAD HTL. Through this process, a large area module of $12.5 \text{ cm} \times 13.5 \text{ cm}$ was realized, and combined with the newly developed laser ablation process, the PCE more than 10% with a power output of 1.7 W was obtained. The development of the large area PSCs got advanced since it exhibited high geometrical fill factor, impressive PCE and low-temperature solution processing. In 2018, Luo and co-workers [71] used graphene as the transparent anode, carbon nanotube as the cathode, spiro-OMeTAD as the HTM to fabricate all-carbon electrode based PSCs that yielded a final PCE of 11.9%. In 2019, Zhou et al. [43] reported all-inorganic CsPbI_2Br perovskite solar cells which was processed at low temperature. They used spiro-OMeTAD to construct HTL, and at the same time thermally evaporated a thin film of MoO_3 (8 nm) on it as an interface layer that could suppress carrier recombination and extract charge carrier efficiently. The optimized cells demonstrated a high PCE up to 14.05%. Wang et al. [44] also reported an inorganic PSCs using spiro-OMeTAD as HTM. They synthesized highly crystalline $\beta\text{-CsPbI}_3$ films

Table 2 Photovoltaic characteristics of organic HTM-based perovskite solar cells

HTM	Type	Device structure	$V_{oc}/$ V	$J_{sc}/$ (mA·cm ⁻²)	FF	PCE/ %	Refs.
Spiro-OMeTAD	Planar n-i-p	ITO/SnO ₂ /PVSK/PEAI/spiro-OMeTAD/Au	1.160	24.90	0.8140	23.56	[42]
		ITO/SnO ₂ /PVSK/spiro-OMeTAD/Au	1.120	23.86	0.8060	21.64	[41]
		FTO/c-TiO ₂ /CHI-CsPbI ₃ /spiro-OMeTAD/Ag	1.110	20.23	0.8200	18.40	[44]
		ITO/SnO ₂ /CsPbI ₂ Br/Spiro-OMeTAD/MoO ₃ /Ag	1.120	15.40	0.8150	14.05	[43]
	Mesoporous n-i-p	FTO/cp-TiO ₂ /mp-TiO ₂ /PVSK/spiro-OMeTAD/Au	1.162	23.78	0.7880	22.00	[45]
		FTO/cp-TiO ₂ /mp-TiO ₂ /PVSK/spiro-OMeTAD/Au	1.120	23.98	0.7962	21.38	[47]
		FTO/cp-TiO ₂ /mp-TiO ₂ /PVSK/spiro-OMeTAD/Au	1.160	24.60	0.7300	20.80	[40]
		FTO/cp-TiO ₂ /mp-TiO ₂ /PVSK/spiro-OMeTAD(using Mg-TFSI ₂)/Au	1.091	22.62	0.7670	18.93	[46]
		FTO/cp-TiO ₂ /mp-TiO ₂ /PVSK/spiro-OMeTAD(using Ca-TFSI ₂)/Au	1.084	22.54	0.7650	18.69	
		FTO/cp-TiO ₂ /mp-TiO ₂ /PVSK/po-spiro-OMeTAD/Au	1.020	21.20	0.7760	16.70	[39]
PTAA	Planar p-i-n	ITO/PTAA/PVSK/C ₆₀ /BCP/Cu	1.170	24.10	0.8160	23.00	[51]
		ITO/PTAA/PVSK/PCBM/BCP/Ag	1.262	20.70	0.8010	20.70	[50]
	Mesoporous n-i-p	FTO/cp-TiO ₂ /mp-TiO ₂ /PVSK/PTAA/Au	1.110	25.00	0.8170	22.60	[48]
		FTO/cp-TiO ₂ /mp-TiO ₂ /PVSK/PTAA/LAD/Au	1.120	23.06	0.7900	20.32	[49]
		FTO/cp-TiO ₂ /mp-TiO ₂ /PVSK/PTAA/ Au	1.050	22.35	0.8100	19.01	[34]
PEDOT:PSS	Planar p-i-n	ITO/PEDOT:PSS/PTAA/PVSK/PCBM/Ag	1.070	21.58	0.8259	19.04	[56]
		ITO/PEDOT:PSS/PVSK/PC ₆₁ BM/Ag	1.040	22.22	0.8000	18.46	[60]
		ITO/PEDOT:PSS/PVSK/PCBM/Au	1.100	20.90	0.7900	18.20	[52]
		ITO/PEDOT:GO/PVSK/PCBM/ZnO/Ag	1.020	21.55	0.8230	18.09	[55]
		ITO/PEDOT:PSS/PVSK/PCBM/BCP/Ag	1.020	21.93	0.7600	17.22	[54]
		FTO/PEDOT:PSS/GQDs/PVSK/PC ₆₁ BM/Ag	1.002	21.41	0.7531	16.16	[59]
		ITO/PEDOT:PSS/SrGO/PVSK/PCBM/BCP/Ag	1.040	19.39	0.8048	16.01	[58]
		ITO/m-PEDOT:PSS/PVSK/PC ₆₁ BM/Al	1.110	18.44	0.7600	15.56	[53]
		ITO/PEDOT:PSS-CuSCN/PVSK/PCBM/C ₆₀ /LiF/Al	1.020	19.10	0.7850	15.30	[57]
P3HT	Mesoporous n-i-p	FTO/cp-TiO ₂ /mp-TiO ₂ /NBH/WBH/P3HT/Au	1.152	24.88	0.8140	23.30	[35]
		FTO/cp-TiO ₂ /mp-TiO ₂ /PVSK/P3HT/Au	1.024	23.19	0.6860	16.27	[62]
		FTO/cp-TiO ₂ /mp-TiO ₂ /PVSK/P3HT/Au	0.970	23.90	0.6200	14.40	[61]
DM	Mesoporous n-i-p	FTO/cp-TiO ₂ /mp-TiO ₂ /PVSK/DM/Au	1.144	24.91	0.8129	23.20	[65]
TAT- ^t BuSty	Planar n-i-p	FTO/SnO ₂ /PVSK/TAT- ^t BuSty/Au	1.150	22.10	0.8000	20.30	[68]
X26	Mesoporous n-i-p	FTO/cp-TiO ₂ /mp-TiO ₂ /PVSK/X26/Au	1.110	24.30	0.7500	20.20	[64]
X36	Mesoporous n-i-p	FTO/cp-TiO ₂ /mp-TiO ₂ /PVSK/X36/Au	1.060	23.70	0.7600	18.90	
FDT	Mesoporous n-i-p	FTO/cp-TiO ₂ /mp-TiO ₂ /PVSK/FDT/Au	1.148	22.70	0.7600	20.20	[63]
SCZF-5	Planar n-i-p	FTO/TiO ₂ /PVSK/SCZF-5/MoO ₃ /Ag	1.110	24.40	0.7400	22.10	[66]
TTE	Planar n-i-p	ITO/SnO ₂ /PVSK/TTE-2/Au	1.110	23.26	0.7753	20.04	[67]
		ITO/SnO ₂ /PVSK/TTE-1/Au	1.030	18.46	0.7168	13.68	
PTEG	Planar n-i-p	FTO/SnO ₂ /Cs-PVSK/PTEG/Au	1.140	22.50	0.7700	19.80	[69]
	Mesoporous n-i-p	FTO/cp-TiO ₂ /mp-TiO ₂ /Cs-PVSK/PTEG/Au	1.090	22.70	0.7540	18.60	

as light absorbing layer and further optimized it by surface treating with choline iodide, resulting in a best PCE of 18.4% for corresponding devices.

Although outstanding PCE of PSCs with spiro-OMeTAD has been clearly demonstrated, the dopants like Li-TFSI and tBP readily degrade both the organic HTL and

Fig. 6 Structure and photovoltaic properties of top-performance PSCs. **a** Spiro-OMeTAD-based PSCs that achieved a PCE of 23.56% (from left to right being device structure, J - V curve and external quantum efficiency (EQE) curve, respectively). Reproduced with permission from Ref. [42]. Copyright 2019 Springer Nature. **b** P3HT-based PSCs that achieved a PCE of 23.3% (from left to right being device structure, energy level diagram, J - V curve and EQE curve, respectively). Reproduced with permission from Ref. [35]. Copyright 2019 Springer Nature. **c** DM-based PSCs (from left to right being device structure, comparison diagram of DM and spiro-OMeTAD energy levels, J - V curve and EQE curve, respectively). Reproduced with permission from Ref. [65]. Copyright 2018 Springer Nature

the perovskite films, declining the long-term stability of PCEs. So, there are great number of researches focusing on other dopants with better stability. In 2018, Seo et al. [45] synthesized a Zn-TFSI₂ to replace Li-TFSI in a conventional (n-i-p) PSCs. The spiro-OMeTAD based devices with Zn-TFSI₂ showed a much higher PCE of 22.0% than that using Li-TFSI. Moreover, compared to the devices with Li-TFSI, it outperformed in operational stability and capability of effective resistance to moisture for that with Zn-TFSI₂. In 2020, Pham et al. [46] used more hydrophobic Mg-TFSI₂ and Ca-TFSI₂ additives to replace Li-TFSI. They found that increased hydrophobicity helped to keep the coordination complexes between the TFSI-salts and tBP stable, which could impede additive aggregation and hydration, improving hole mobility and moisture-resistance of HTLs. As a consequence, the spiro-OMeTAD based PSCs with more hydrophobic dopants (together with tBP and FK209) exhibited a best PCE of more than 20% and good stability (83% of initial efficiency was still saved after aging in ambient air for 193 days). Sathiyar et al. [47] designed a dual functional dopant PFPPY that could take place of both tBP and FK209. The PSCs with spiro-OMeTAD doped by Li-TFSI and 15% PFPPY

demonstrated a remarkable PCE of 21.38% and greatly improved stability (maintaining more than 90% of its original PCE after aging in 40%–50% relative humidity for 600 h).

2.2 PTAA

Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) is also a common HTM used in PSCs. Similar with spiro-OMeTAD, it only works effectively in the presence of some additives, leading to instability issue. In 2017, Yang et al. [48] employed PTAA and dopants of Li-TFSI, tBP as the HTMs to fabricate mesoporous PSCs consisting of a defect-engineered thin perovskite layer. They finally released the highest PCE of 22.1% at the time and a high PCE of 19.7% for 1 cm² cells. To promote the stability of PTAA-based PSCs, considerate efforts have been made. In 2018, Luo et al. [34] developed a fluorine-containing hydrophobic Lewis acid dopant (LAD) and used it to replace tBP and Li-TFS. The mesoporous PSCs with PTAA and LAD as HTMs demonstrated an excellent fill factor up to 0.81 and a higher PCE of 19.01% than that of 17.77% for the devices using Li-TFSI/tBP doped PTAA.

Significantly, much better long-term stability and lower $J-V$ hysteresis was observed for the devices with LAD. Subsequently, in 2020, they explored the LAD doping route and reported an infiltrated diffusion doping (INDD) way [49]. In this study, PTAA was deposited at first and then LAD was deposited from the solution using orthogonal solvent with respect to the PTAA. The optimal PSCs processed by INDD method exhibited a high PCE of 20.32% that 93% of it still retained up to 1500 h in ambient condition without any encapsulation, indicating outstanding long-term stability.

PTAA is also used as HTM in the inverted (p-i-n) PSCs, which is usually prepared with [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM) as ETM rather than PEDOT:PSS. The devices with this configuration normally show a long operating lifetime and nearly no hysteresis is observed. Nevertheless, the PCE is relatively low compared with that of devices based on the conventional (n-i-p) structure. For example, in 2019, Liu et al. [50] fabricated a planar $CH_3NH_3PbI_3$ PSCs using PTAA as HTM and PCBM as ETM, obtaining a V_{OC} up to 1.26 V and a PCE of more than 20% by optimizing perovskite precursors and interfacial layer between PTAA and PCBM. In 2020, Zheng and co-workers [51] showed the use of surface-anchoring alkylamine ligands (AALs) in inverted PSCs. They found that the addition of long-chain AAL to the precursor solution helped to inhibit the recombination of non-radiative carriers and improve the photoelectric performance of the mixed-cation mixed-halide perovskite film, which resulted in a certified stable PCE of 22.3% and the best lab-measured PCE of 23%.

2.3 PEDOT:PSS

PEDOT:PSS is also a commonly used HTM in inverted (p-i-n) planar PSCs. PEDOT:PSS-based PSCs show advantages of simple preparation and low hysteresis. But the photovoltaic performance including V_{OC} , short circuit current (J_{SC}) and stability are relatively low because of the huge energy barrier between PEDOT:PSS and the perovskite layers as well as the high acidity of the PEDOT:PSS solution. In 2015, Heo and co-workers [52] prepared inverted PSCs by spin-coating the perovskite solution via a single-step method. These devices in configuration of ITO/PEDOT:PSS/MAPbI₃/PCBM/Au demonstrated a higher PCE of 18.1%, less hysteresis, longer charge carrier lifetime (τ_n), an improved diffusion coefficient (D_n) and better stability compared with that of conventional FTO (fluorine doped tin oxide)/TiO₂/MAPbI₃/PTAA:tBP + Li-TFSI/Au planar PSCs. Many researches were also done to modify or dope PEDOT:PSS. In 2017, Zuo and Ding [53] tried to add polymer electrolyte PSS-Na into regular PEDOT:PSS. The modified

PEDOT:PSS had higher work function and better matched energy level to the perovskite than the regular one, inducing increase in V_{OC} from 0.96 to 1.11 V and PCE from 12.35% to 15.56% for corresponding devices. Liu and co-workers [54] reported the effect of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) dopant on the PEDOT:PSS. It was found that low concentration doping of F4-TCNQ could enhance the electrical conductivity and make energy level of the PEDOT:PSS HTL more matching with perovskite layer. Finally, the best PCE of PSCs was improved from 13.30% to 17.22% with doping of F4-TCNQ. In 2018, Yu and co-workers [55] selected graphene oxide (GO) doped PEDOT:PSS (PEDOT:GO) as HTM to construct inverted PSCs. The superior electrical and optical performance of PEDOT:PSS were obtained with doping of graphene oxide. The PSCs with PEDOT:GO achieved a PCE up to 18.09% and outstanding long-term stability (maintained 80% of the original PCE after 25 days). In 2019, Wang et al. [56] proposed to introduce an ultrathin PTAA layer between PEDOT:PSS layers and the perovskite to realize an energy band alignment in PSCs. The role of ultrathin PTAA layer was also determined to suppress interfacial recombination and accelerate hole transfer. Finally, they obtained a best PCE of 19.04% with fill factor (FF) of 82.59% and J_{SC} of 21.38 mA·cm⁻². In 2020, Xu et al. [57] employed a CuSCN-doped PEDOT:PSS as HTM to fabricate inverted PSCs that reached a PCE of 15.3% with greatly advanced stability. Mann et al. [58] fabricated inverted PSCs by applying PEDOT:PSS/SrGO (sulfonic acid functionalized graphene oxide) layer in a low temperature and solution process, achieving a PCE up to 16.01% and excellent long-term stability. Li et al. [59] mixed graphene quantum dots into PEDOT:PSS and used this composite HTM in PSCs that showed an average PCE of 15.24% and a best PCE of 16.15%. Reza and co-workers [60] reported a facile solvent-engineered approach that could remove the predominant PSS in PEDOT:PSS layer. With the modification, PEDOT:PSS layer became non-wetting, which facilitated the formation of large perovskite crystalline domains. The optimal PSCs exhibited shorter charge transport time, higher charge carrier lifetime and lower transfer impedance than others, leading to a PCE of 18.18% with largely improved stability.

2.4 P3HT

Poly(3-hexylthiophene) (P3HT) is also a prospective organic HTM for PSCs because of its high charge carrier mobility, suitable band gap matched in maximum with the sun light spectrum and low cost. However, the devices taking P3HT as HTMs usually show a low conversion efficiency because of relatively low conductivity. Hence, great number of studies has been made to promote the

conductivity of P3HT. In 2016, Zhang et al. [61] introduced F4TCNQ as an effective p-type dopant in P3HT that induced a dramatic improvement of the bulk conductivity of P3HT. The mesoscopic PSCs with doped P3HT demonstrated a PCE of 14.4% that was much higher than 10.3% for pristine P3HT-based devices. In 2017, Nia et al. [62] synthesized P3HT with different molecular weight (MW) and studied their effect on the performance of PSCs. It was demonstrated that the devices based on P3HT with high MW of 124 kDa outperformed others, showing an average PCE of 16.2%. The superior performance was attributed to the improvement of the P3HT absorbance and the charge carrier lifetime along with MW increase. Though the PCE of P3HT-based PSCs was improved, it was yet much lower compared with the PCE of the spiro-OMeTAD or PTAA-based PSCs. An exceptional breakthrough in PCE of 22.7% was obtained in 2019. Jung et al. [35] prepared PSCs applying pristine P3HT as HTM. Specially, the perovskite active layer in these PSCs was consisted of a narrow-bandgap-halide (NBH) light absorbing layer and an ultrathin wide-bandgap halide stacked onto NBH. The devices based on this double-layered halide architecture (DHA) showed a certified PCE of 22.7%, a maximum PCE up to 23.3% with negligible hysteresis of $\pm 0.51\%$ and good stability. The structure and photovoltaic performance of the device are shown in Fig. 6. Moreover, they also demonstrated that both P3HT deposition and DHA configuration could be achieved in large area modules, which exhibited a PCE of 16%.

2.5 Other organic HTMs

Besides the typical organic HTMs mentioned above, there are various organic molecules synthesized to use as HTM in PSCs [72–74]. Some of them make an impressive PCE achievable and some show good stability or low cost. Here, we will mainly discuss highly efficient HTMs in PSCs.

Saliba and co-workers [63] prepared a novel HTM of 2',7'-bis(bis(4-methoxyphenyl)amino)spiro[cyclopenta[2,1-b:3,4-b']dithiophene-4,9'-fluorene] (FDT) in 2016. The devices based on FDT with dopants of Li-TFSI, FK209, and tBP exhibited a high PCE up to 20.2%. They also stressed that FDT could potentially replace the traditional spiro-OMeTAD because it could dissolve well in toluene, which was less toxic and cheaper than chlorobenzene. In 2018, Zhang et al. [64] developed two kinds of organic molecules with spiro[fluorene-9,9'-xanthene] (SFX)-based pendant groups. When the obtained X26 and X36 took place of the spiro-OMeTAD to form HTL, a better conductivity, improved thin-film surface morphology and more suitable energy levels were observed. The PSCs using doped X26 (Li-TFSI, tBP, and FK209) exhibited a high PCE up to 20.2% and great stability. Jeon and co-workers

[65] synthesized a fluorene-terminated HTM ($N^2, N^{2'}, N^7, N^{7'}$ -tetrakis(9,9-dimethyl-9H-fluorene-2-yl)- $N^2, N^{2'}, N^7, N^{7'}$ -tetrakis(4-methoxyphenyl)-9,9'-spirobi[fluorene]-2,2',7,7'-tetraamine) (DM) with a high-glass transition temperature and fine-tuned energy level. This material (together with tBP and Li-TFSI) was utilized in a mesoporous PSCs having $(FAPbI_3)_{0.95}(MAPbBr_3)_{0.05}$ as perovskite material. The optimal devices showed a certified PCE up to 22.6% and a best PCE of 23.2% as well as excellent long-term stability after annealing at 60 °C for 500 h. The structure and photovoltaic performance of the device are shown in Fig. 6. In 2019, Zhu et al. [66] designed a new carbazole-based single-spiro-HTM named SCZF-5. Then they fabricated PSCs with different HTMs of SCZF-5, spiro-OMeTAD and another single-spiro material SAF-5. All the HTMs were doped with tBP and Li-TFSI. In comparison, the SCZF-5 PSCs exhibited a more impressive PCE up to 20.10% than that of spiro-OMeTAD (19.11%) and SAF-5 (13.93%) based devices. This could be assigned to the rigid backbone of SCZF-5, improving hole-transporting capability and decreasing HOMO level of the HTL. Shen et al. [67] reported an efficient dopant-free HTM TTE-2 with semi-locked tetra-thienylethene (TTE) as the core. By comparing it with the TTE-1 that was made on basis of unlocked TTE core, they initiated a hybrid concept between planar and orthogonal molecular conformation, which could result an unprecedented balance between morphology modulation and charge mobility. The TTE-2-based conventional planar PSCs demonstrated a maximum PCE up to 20.04% and good stability.

3 Inorganic HTMs

Though the PSCs based on typical organic HTMs exhibit excellent PCE, the stability issue is still a big challenge. To take advantage of dopant-free organic HTMs is helpful to improve the stability, while to utilize inorganic materials can be a more effective strategy. Inorganic HTMs usually have great advantages of simple preparation, good chemical stability, high hole mobility and low cost, which makes it a potential candidate for organic HTMs to be used in stable PSCs [75–77]. Table 3 shows the physicochemical properties of the common inorganic HTMs [31, 78]. But the PCE of inorganic HTM-based PSCs is relatively low and only a few research groups have achieved the PCE higher than 20%.

3.1 Copper oxide

Cuprous oxide (Cu_2O) and cupric oxide (CuO) are typical inorganic HTMs in PSCs. They have high-absorption

Table 3 Physicochemical properties of several inorganic HTMs

Parameters	Cu ₂ O [31]	CuSCN [31]	CuI [31]	NiO [31]	MoS ₂ [78]
Electron mobility/(cm ² ·V ⁻¹ ·s ⁻¹)	200	100	100	12	100
Hole mobility/(cm ² ·V ⁻¹ ·s ⁻¹)	80.0	25.0	43.9	2.8	150.0
Band gap/eV	2.17	3.60	3.10	3.80	1.29
Conduction band effective density of states/cm ⁻³	2.0×10^{17}	2.2×10^{19}	2.8×10^{19}	2.8×10^{19}	2.2×10^{18}
Valence band effective density of states/cm ⁻³	1.1×10^{19}	1.8×10^{18}	1.0×10^{19}	1.0×10^{19}	1.8×10^{19}
Acceptor concentration/cm ⁻³	1.0×10^{18}	1.0×10^{18}	1.0×10^{18}	1.0×10^{18}	1.0×10^{17}
Electron affinity/eV	3.2	1.7	2.1	1.46	4.2

coefficient except the other advantages in common and have been widely used in inverted PSCs by replacing PEDOT:PSS. In 2016, Yu et al. [79] reported a planar inverted PSCs with an ultrathin p-type Cu₂O film prepared in a facile thermal oxidation way. They optimized the film thickness by controlling sputtering time and the best device with PCE of 11.0% was obtained, which could be owed to the good energy level alignment with CH₃NH₃PbI₃, high hole mobility and long lifetime of photo-excited carriers of ultrathin Cu₂O. Sun et al. [80] produced a CuO_x layer in planar inverted PSCs by a facile solution-processed method. The formed CuO_x layer was smooth and highly transparent in the visible region. A PCE of 17.1% was demonstrated for PSCs based on CuO_x layer, as well as an excellent stability in air (maintaining nearly 90% of the original PCE after 200 h). They also explored the influence of the ratio of Cu²⁺ and Cu⁺ in the CuO_x film on device performance and found that the devices with different CuO_x films showed similar PCE, but the FF decreased slightly with the increasing of CuO content. Rao et al. [81] reported a new Cl doping method that could improve the morphology of perovskite film, resulting in increase of hole mobility and reduction of both the intrinsic defects and charge carriers recombination. The PSCs utilizing CH₃NH₃PbI_{3-x}Cl_x as light absorbing layer and CuO_x film as HTL showed an excellent PCE of 19%. In 2020, Tseng et al. [82] fabricated an inverted PSCs employing Cu₂O as HTM and SiO₂ as ETM. They successfully reduced the thickness of Cu₂O HTL and SiO₂ ETL by a novel hetero-contact synthesis engineering, improving the V_{OC} of devices. Meanwhile they employed a gallium-doped zinc oxide layer as transparent conducting oxide film to decrease the parasitic absorption. As a result, a PCE of 18.4% was obtained.

Copper oxide was used in conventional (n-i-p) PSCs as well. In 2018, Chen et al. [83] made Cu/Cu₂O film by ion beam sputtering and introduced it between Ag electrode and spiro-OMeTAD layer in mesoporous PSCs. The PSCs achieved a best PCE of 17.11%, ascribing to Cu/Cu₂O films with the high hole mobility. Meanwhile the durability

of PSCs was also improved because Cu/Cu₂O films could prevent moisture and Ag penetrating into the perovskite layer. However, it was pointed out that the perovskite layer would be damaged during the high energy sputtering of the Cu/Cu₂O composite layer, thus the spiro-OMeTAD layer had to be present. In 2019, Liu and co-workers [84] proposed a simple method by that the surface modification of cuprous oxide (Cu₂O) quantum dots could be done with a silane coupling agent. The modified Cu₂O layer could be directly deposited on the perovskite layer and the corresponding PSCs performed a higher PCE up to 18.9% in contrast with that of 11.9% for unmodified Cu₂O-based PSCs.

3.2 Copper(I) thiocyanate (CuSCN)

Besides the advantages in common, for example, high chemical stability and simple preparation, CuSCN is of excellent transparency in the visible spectrum range. Nevertheless, the solvent of diethyl sulfide (DES) that is commonly used in solution processing of CuSCN can induce deterioration of the perovskite layer, limiting the further application of CuSCN in n-i-p PSCs. Therefore, researchers tried to fabricate CuSCN-based PSCs with p-i-n configuration. In 2015, Ye et al. [85] prepared CuSCN layer by electrodeposition and subsequently deposited CH₃NH₃PbI₃ film on it via a fast deposition-crystallization way. The formed perovskite films exhibited small interface contact resistance and low surface roughness, making the CuSCN-based PSCs achieve an average PCE of 15.6% and the highest PCE up to 16.6% that could be attributed to the high hole mobility of CuSCN HTL as well.

In addition, it has been proved that the damage to perovskite layer occurring in the solution processing of CuSCN for n-i-p PSCs could be effectively reduced when some special strategies were adopted. As a result, the PCE has reached up to be more than 20% through the overall optimization. Jung and co-workers [86] made a low-temperature solution-processed CuSCN HTM and used it in mesoporous PSCs in 2016. The produced CuSCN

possessed a highly stable crystalline structure even if at high temperature and the devices with it exhibited a stable PCE of 15.9% and a maximum PCE up to 18.0%. It also showed superior thermal stability as approximate 60% of the original PCE was maintained after annealing at 125 °C in air with 40% humidity for 2 h, while that of only 25% was kept for the spiro-OMeTAD-based devices. Arora and co-workers [87] used a fast solvent removal procedure to reduce the damage to the perovskite layer that was induced by DES in 2017. Compact and highly conformal CuSCN layers were successfully obtained that could rapidly extract and collect carriers. The mesoporous PSCs with CuSCN as HTL yielded a PCE over 20% and exhibited high thermal stability. However, the operational stability was low due to the potential-induced degradation of the CuSCN/Au contact and thereby a graphene oxide (rGO) spacer layer was inserted between CuSCN and Au. Consequently, the devices with CuSCN and rGO achieved a PCE of 20.4%, which was almost as good as that of spiro-OMeTAD-based devices (20.8%). The structure and

photovoltaic performance of the device are shown in Fig. 7. Significantly, a much higher operational stability was observed comparing with that of spiro-OMeTAD-based devices under both continuous full-sun illumination and thermal stress. In 2019, Yang et al. [88] succeeded in improving V_{OC} of CuSCN-based PSCs by introducing various functional molecules on the surface of MAPbI₃ layer to passivate the defects and improve the contact between MAPbI₃ and CuSCN layers. When a mixture of 3-pyridyl isothiocyanate (Pr-ITC) and phenylene-1,4-diisothiocyanate (Ph-DITC) were utilized, the V_{OC} of CuSCN-based PSCs increased up to more than 40 mV, resulting in an average PCE of 18.57% and highest PCE up to 19.17%. In addition, the devices with such interfacial modification also showed better long-term stability and less $J-V$ hysteresis in comparison to that of pristine devices. Kim et al. [89] introduced polydimethylsiloxane (PDMS) as a polymeric interlayer in CuSCN-based PSCs to prevent interfacial degradation and improve both conversion efficiency and stability. They identified that PDMS could

Fig. 7 Structure and photovoltaic properties of top-performance PSCs. **a** CuSCN-based PSC that achieved a PCE of 20.4% (from left to right being device structure, $J-V$ curve and EQE curve, respectively). Reproduced with permission from Ref. [87]. Copyright 2017 American Association for the Advancement of Science. **b** NiO_x-based PSC that achieved a PCE of 20.5% (from left to right being device structure, energy level diagrams, $J-V$ curves and EQE curves of devices with different Cu contents, respectively). Reproduced with permission from Ref. [99]. Copyright 2017 The Royal Society of Chemistry. **c** MoS₂-based PSC that achieved a PCE of 20.43% (from left to right being device structure, energy level diagrams and $J-V$ curves of devices with different MoS₂ thicknesses, respectively). Reproduced with permission from Ref. [78]. Copyright 2018 IOP Publishing Ltd

combine with perovskite and CuSCN in chemical bonds, which could enhance the hole transporting at the interface and passivate the interfacial defects. The PSCs with the PDMS layer exhibited the highest PCE of over 19% with improved stability against both humidity and heat.

3.3 Copper(I) iodide

CuI is another common inorganic HTM with inherent properties of low produce cost, large bandgap, good chemical stability, and high hole mobility. In 2014, Christians et al. [90] firstly used CuI in mesoporous PSCs and obtained a promising PCE of 6.0%. Though the V_{OC} of CuI-based devices was lower compared with the spiro-OMeTAD-based devices, the FF was superior because of CuI exhibited 2 orders of magnitude higher electrical conductivity than spiro-OMeTAD. Sepalage et al. [91] proposed a planar n-i-p PSCs with CuI as HTM in 2015. The devices showed an average PCE of $5.8\% \pm 0.8\%$ and a maximum PCE of 7.5% without distinct hysteresis. Chen et al. [92] prepared inverted (p-i-n) planar PSCs with low-cost and solution-processed CuI or PEDOT:PSS as HTM, respectively. By comparison, there was no obvious improvement of PCE observed (13.58% for CuI-based devices and 13.28% for PEDOT:PSS-based devices), while the device stability was greatly improved along with replacing PEDOT:PSS with CuI. In 2017, Li et al. [93] constructed mesoporous PSCs employing modified TiO_2 as ETL and CuI film as HTL. Specifically, they used Na species to modify TiO_2 layer so as to improve the electron conductivity and mobility of ETL, meanwhile they adopted a facile spray-deposition method to prepare CuI layer. The devices demonstrated a maximum PCE up to 17.6%, great stability and depressed hysteresis. In 2019, Cao and co-workers [94] designed hybrid CuI/Cu nanostructure by partial iodation of Cu nanowires and used it as HTM in inverted (p-i-n) PSCs. The inner Cu favored rapid transfer of the extracted charges and the outer CuI favored effective charge extraction. Moreover, they used a mixture of PCBM and ZnO nanoparticles as ETL to improve the stability of devices. Finally, the devices obtained a maximum PCE up to 18.8% and good long-term stability against humidity.

3.4 Nickel oxide (NiO_x)

NiO_x shows a deep valence band, high chemical stability and etc. So far, the PSCs with NiO_x HTM has achieved a high PCE of more than 20% since the first application in conventional (n-i-p) PSCs. In 2014, Wang et al. [95] studied the effect of oxygen doping in low-temperature sputtered NiO_x film on device performance. They found that there are Ni^{3+} formed during the oxygen doping process and proper Ni^{3+} can improve the PCE of PSC devices,

but excessive Ni^{3+} content will adversely affect performance. With adequate doping under 10% oxygen flow ratio, they achieved a PCE of 11.6%. Xu et al. [96] reported PSCs consisting of carbon as electrode, mesoporous NiO and TiO_2 layers as hole and electron selective contacts, respectively, and a mesoporous ZrO_2 layer as a space separator in 2015. A PCE of 14.9% was achieved finally. Cao et al. [97] employed Al_2O_3 as space separator and prepared NiO -based PSCs in the similar structure, achieving a PCE of 15.03%. Afterward, considerable studies were kept on making in order to promote photovoltaic performance of NiO -based PSCs and it was found that inverted (p-i-n) devices were more efficient than conventional (n-i-p) ones. Xie et al. [98] reported the PSCs with FTO/ NiO_x /FAPbI₃/PCBM/ TiO_x /Ag structure. FA-based perovskite film with high crystallinity was obtained by adding methylammonium chloride (MACl) that could assist vertical recrystallization of perovskite in 2017. It resulted in reducing carrier recombination of perovskite layer, and thus, high PCE of 20.65%. Besides, the devices showed great thermal stability and light-soaking stability because of low MA content, phase-pure morphology and the highly crystalline in perovskite films. Yue et al. [99] presented a series of strategies for effectively regulating of the charge extraction in inverted NiO_x -based PSCs. With doping Cl^- into the perovskite layer of $CH_3NH_3PbI_{3-x}Cl_x$, V_{OC} of devices increased. With modification of the aluminum (Al) cathode by zirconium acetylacetonate, doping of copper into the NiO_x HTL and usage of an advanced FTO substrate, the bandgap alignment of devices was improved. This could accelerate the transport rate and reduce the trap states, which was beneficial to extracting the charge carriers. Finally, an excellent PCE up to 20.5% was achieved. The structure and photovoltaic performance of the device are shown in Fig. 7. In 2020, Ru and co-workers [100] found that some molecules with controlled electron affinity could make conductivity of HTMs improved dramatically (more than 10 times) and energy gap between the Fermi level and the valence band decreased, leading to V_{OC} and FF of the PSCs increasing. They chose new 3,6-difluoro-2,5,7,7,8,8-exacyanoquinodimethane (F2HCNQ) molecules and mixed them with NiO_x . The F2HCNQ- NiO_x based PSCs achieved an excellent PCE up to 22.13% with V_{OC} of 1.14 V, J_{SC} of $23.44 \text{ mA}\cdot\text{cm}^{-2}$ and FF of 82.80%. Moreover, the flexible solar cells and modules using F2HCNQ- NiO_x as HTM achieved a PCE up to 20.01% and 12.4%, respectively.

3.5 Transition metal dichalcogenides (TMDs)

Two-dimensional transition metal chalcogenides are one of promising HTMs because of their high hole mobility, among which MoS_2 is the most widely used one. In recent

years, the MoS₂-based PSCs have gained much more attention and achieved an excellent PCE of over 20%. In 2016, Kim et al. [101] used atomically thin two-dimensional materials of MoS₂, WS₂, and graphene oxide (GO) as HTM in inverted PSCs. MoS₂ and WS₂ layers were synthesized in a chemical deposition way. The devices with WS₂, MoS₂, and GO exhibited a PCE of 8.02%, 9.53% and 9.62%, respectively, which was only slightly lower than 9.93% of the spiro-OMeTAD-based PSCs. In 2017, Huang et al. [102] prepared MoS₂ and WS₂ by exfoliating the corresponding bulk materials with lithium intercalation reaction and fabricated inverted (p-i-n) PSCs. They demonstrated that the phase conversion of TMDs had an important effect on the properties of devices and that based on 1T-rich TMDs without heating showed much higher PCE than that with heated TMDs. Finally, a PCE of 15.00% and 14.35% was achieved for WS₂-based and MoS₂-based devices, respectively. Moreover, the stability of these devices was higher compared to that of PEDOT:PSS-based devices. In 2018, Kohnehpoushi et al. [78] reported PSCs with a configuration of ITO/MoS₂/CH₃NH₃PbI₃/TiO₂/Ag and studied the effect of thickness of MoS₂ on the conversion efficiency. They found that a single sheet (0.67 nm) MoS₂ could effectively promote the PCE up to 20.43% and the devices with two-layers MoS₂ (1.34 nm) showed the similar PCE of 20.52%, yet further increase in the MoS₂ thickness caused decrease of the device performance. The structure and photovoltaic performance of the device are shown in Fig. 7. Najafi et al. [103] used hybrids of reduced graphene oxide (RGO) and MoS₂ quantum dots (QDs) as HTM in mesoporous PSCs. It was demonstrated that MoS₂ QDs could offer both electron-blocking and hole-extracting properties, while the van der Waals hybridization of MoS₂ QDs with RGO could effectively homogenize the deposition of HTL, making an average PCE of 18.8% and a best PCE up to 20.12% for the hybrids-based devices.

3.6 Other inorganic HTMs

Besides these materials discussed above, there are many other inorganic HTMs which have been studied, such as CuS, CuCrO₂, MoO_x, WO_x. In this section, we will introduce some of them that were employed in high-performing PSCs that are summarized in Table 4 [78–94, 96–109]. In 2017, Ye and co-workers [104] reported a new p-type conductor Cu (thiourea)I [Cu(Tu)I] in inverted PSCs. It could effectively passivate the trap states of perovskite film and take part in constructing the p-i bulk heterojunctions with perovskite, leading to depletion width broaden that was beneficial for reducing charge carrier recombination and facilitating hole transporting. Consequently, the devices reached a PCE of 19.9%. In 2018, Zhang and co-

workers [105] introduced the semi-conductive antimonene nanosheets (SANs) into inverted planar PSCs with ITO/PTAA/SANs/CH₃NH₃PbI₃/PC₆₁BM/Bphen/Al structure. The SANs were fabricated by a liquid-phase exfoliation method and could accelerate the hole transfer and extraction rate at the perovskite/HTL interface, making the devices possess a high PCE of 20.05%. In 2019, Li et al. [106] reported the usage of an eco friendly and low-cost MnS film as HTL in mesoporous PSCs. MnS film had the characteristics of high hole mobility, suitable band alignment and optical transparency. The devices based on it performed a PCE of 19.86% and superior stability (maintaining more than 90% of original PCE for 1000 h after exposure to air with a relative humidity of 80% without any encapsulation). Taghavinia et al. fabricated planar n-i-p PSCs employing solution-processed copper indium gallium disulfide (CIGS) nanocrystals as HTM [107]. They studied the influence of Ga concentration on the Cu(In_{1-x}Ga_x)S₂ composition on the device performance. Under the optimal condition, the Cu(In_{0.5}Ga_{0.5})S₂-based PSCs achieved the maximum PCE of 15.6% with great stability (maintaining 70% of initial PCE for 90 days after aging in 50% relative humidity and in the dark conditions). Then in 2020, they reported a similarly structured-devices with carbon composite as electrode and CuIn_{0.75}Ga_{0.25}S₂ as HTM. The PCE of the devices was 15.9% [108].

4 Conclusion

In this article, a variety of reported HTMs in PSCs was reviewed. Among them, organic and inorganic HTMs were highlighted and discussed in detail. It was found that PSCs with typical organic HTMs usually exhibited higher PCE than that with inorganic HTMs, while adding dopants were indispensable for most of the effective organic HTMs so as to improve their conductivity and/or hole mobility, inducing instability of high-performing organic HTM-based devices. Though their dopant-free organic HTMs were successfully synthesized and the corresponding devices showed both promising PCE and good stability, organic spiro-OMeTAD was still dominant in all the HTMs as the state-of-art PSCs based on it could achieve a PCE which was comparable to that of silicon-based solar cells. Therefore, there are still a lot of room for further development of organic HTMs, for example, designing novel spiro-OMeTAD analoges with improved conductivity. For inorganic HTMs, the highly efficient PSCs with it could reach a PCE over 20%, and more importantly, they showed superior stability, making inorganic HTMs great potential. How to further improve PCE of inorganic HTMs-based devices by engineering HTMs will be a significant research direction in future.

Table 4 Photovoltaic characteristics of inorganic HTM-based perovskite solar cells

HTM	Type	Device structure	V_{oc}/V	$J_{sc}/(mA \cdot cm^{-2})$	FF	PCE/%	Refs.
CuO_x	Planar p-i-n	ITO/ CuO_x /PVSK/PCBM/ C_{60} /BCP/Ag	1.110	22.50	0.7580	19.00	[81]
		FTO/ Cu_2O /PVSK/ SiO_2 /GZO/Ag	1.120	20.90	0.7860	18.40	[82]
		ITO/ CuO_x /PVSK/ C_{60} /BCP/Ag	0.99	23.20	0.7440	17.10	[80]
		ITO/ Cu_2O /PVSK/PCBM/Ag	0.952	17.50	0.6620	11.03	[79]
	Mesoporous n-i-p	FTO/cp- TiO_2 /mp- TiO_2 /PVSK/ Cu_2O /Au	1.150	22.20	0.7420	18.90	[84]
CuSCN	Mesoporous n-i-p	FTO/cp- TiO_2 /mp- TiO_2 /PVSK/spiro-OMeTAD/ Cu_2O /Ag	1.030	22.46	0.7410	17.11	[83]
		FTO/cp- TiO_2 /mp- TiO_2 /PVSK/CuSCN/rGO/Au	1.112	23.24	0.7820	20.40	[87]
		FTO/cp- TiO_2 /mp- TiO_2 /PVSK/Pr-ITC + Ph-DITC/CuSCN/Au	1.071	23.49	0.7621	19.17	[88]
	Planar n-i-p	FTO/cp- TiO_2 /mp- TiO_2 /PVSK/CuSCN/Au	1.040	23.10	0.7530	18.00	[86]
		ITO/ SnO_2 /PVSK/PDMS/CuSCN/Au	1.017	23.90	0.7830	19.04	[89]
CuI	Planar p-i-n	ITO/CuSCN/PVSK/ C_{60} /BCP/Ag	1.000	21.90	0.7580	16.60	[85]
		FTO/Cu@CuI/PVSK/PCBM/ ZnO /Ag	1.060	23.31	0.7611	18.80	[94]
	Planar n-i-p	FTO/CuI/PVSK/PCBM/Al	1.040	21.06	0.6200	13.58	[92]
		FTO/ TiO_2 /PVSK/CuI/Au	0.780	16.70	0.5700	7.50	[91]
		FTO/cp- TiO_2 /mp- $Na-TiO_2$ /PVSK/CuI/Au	1.030	22.78	0.7500	17.60	[93]
NiO_x	Planar p-i-n	FTO/cp- TiO_2 /mp- TiO_2 /PVSK/CuI/Au	0.550	17.80	0.6200	6.00	[90]
		ITO/ NiO_x /F2HCNQ/PMMA/PVSK/PCBM/BCP/Ag	1.140	23.44	0.8280	22.13	[100]
		ITO/ NiO_x /F4TCNQ/PMMA/PVSK/PCBM/BCP/Ag	1.120	23.35	0.8064	21.07	
		ITO/ NiO_x /F2TCNQ/PMMA/PVSK/PCBM/BCP/Ag	1.100	23.26	0.7882	20.16	
		FTO/ NiO_x /PVSK/PCBM/ TiO_x /Ag	1.100	23.09	0.8140	20.65	[98]
MoS_2	Mesoporous n-i-p	FTO/ NiO_x + 5%Cu/PVSK/ $PC_{61}BM$ /ZrAcac/Al	1.120	23.07	0.7706	20.14	[99]
		FTO/ TiO_2 / Al_2O_3 /PVSK/ NiO/C	0.915	21.62	0.7600	15.03	[97]
		FTO/ TiO_2 / ZrO_2 /PVSK/ NiO/C	0.917	21.36	0.7600	14.90	[96]
		ITO/ MoS_2 /PVSK/ TiO_2 /Ag	0.930	26.25	0.8400	20.53	[78]
		ITO/ MoS_2 /PVSK/ C_{60} /BCP/Al	0.880	20.94	0.7790	14.35	[102]
WS_2	Planar p-i-n	ITO/ MoS_2 /PVSK/PCBM/BCP/LiF/Al	0.960	14.89	0.6700	9.53	[101]
		FTO/cp- TiO_2 /mp- TiO_2 /PVSK/ MoS_2 QDs:rGO/spiro-OMeTAD/Au	1.110	22.81	0.7975	20.12	[103]
		ITO/ WS_2 /PVSK/ C_{60} /BCP/Al	0.970	21.22	0.7300	15.00	[101]
SANs	Planar p-i-n	ITO/ WS_2 /PVSK/PCBM/BCP/LiF/Al	0.820	15.91	0.6400	8.02	[100]
		ITO/PTAA/SANs/PVSK/ $PC_{61}BM$ /Bphen/Al	1.115	23.46	0.7670	20.05	[105]
Cu(Tu)I	Planar p-i-n	ITO/Cu(Tu)I/PVSK/ C_{60} /BCP/Ag	1.130	22.30	0.7890	19.90	[104]
MnS	Mesoporous n-i-p	FTO/cp- TiO_2 /mp- TiO_2 /PVSK/MnS/Au	1.110	23.40	0.7648	19.86	[106]
CuS	Planar p-i-n	ITO/CuS/PVSK/ C_{60} /BCP/Ag	1.020	22.30	0.7120	16.20	[109]
$Cu(In_{0.75}Ga_{0.25})S_2$	Mesoporous n-i-p	FTO/cp- TiO_2 /mp- TiO_2 /PVSK/ $Cu(In_{0.75}Ga_{0.25})S_2/C$	1.080	23.86	0.6200	15.93	[108]
$Cu(In_{0.5}Ga_{0.5})S_2$	Mesoporous n-i-p	FTO/cp- TiO_2 /mp- TiO_2 /PVSK/ $Cu(In_{0.5}Ga_{0.5})S_2/Au$	1.050	21.67	0.6900	15.58	[107]

In summary, the application of different HTMs in PSCs including their advantages and deficiencies were demonstrated. By reviewing the development of HTMs in recent years, we hope to provide some help for exploration of more efficient, more stable and low cost HTMs.

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