

Recent Progress of Hole Transport Layers of Inverted Perovskite Solar Cells

Wei Liu^{1, *}

¹ Department of Physics, University of California, Santa Barbara, Goleta CA, USA

*Corresponding author: wliu491@ucsb.edu

Abstract: Perovskite solar cells, also known as PSCs, have become a potentially viable choice for a source of clean energy. This is especially true for the inverted structure, which boasts high stability and allows for synthesis by solution at low temperatures. In the inverse structure, one of the most important parts is called the hole transport layer, which plays a key role in acting as a substrate and transporting holes. Several studies on high-temperature liquids have been carried out as part of an effort to effectively enhance the device performance of inverted perovskite solar cells (IPSCs). In addition to common organic components, including PEDOT: PSS and PTAA, this paper also provides information regarding inorganic HTL materials, such as NiOx and compounds based on copper. This study discusses in depth the benefits and drawbacks of these four materials, as well as potential avenues for future research and development, such as the application of dopants and various interface optimization methodologies. It may be possible to improve the PCE of IPSCs as well as the stability if HTL materials are modified. This paper provides new researchers with a solid foundation and direction for optimizing HTL materials.

Keywords: Inverted Perovskite, Hole Transport Layer, Organic Materials, Inorganic Materials.

1. Introduction

With the development of science and technology, the living standard of humans has been significantly improved, along with which there is a surging demand for energy. Traditional energy structures are largely composed of fossil fuels, charcoal, and natural gas. However, none of these are sustainable since they are not renewable and cause severe environmental pollution. Solar energy is ideal and clean energy due to its renewability, for which researchers have developed different kinds of solar cells utilizing either the photoelectric effect or photochemical effect. Traditional silicon-based solar cells are extensively studied and successfully achieve commercial use on large scale. However, its production process is generally complicated and maintains high unit cost, for which solar cells based on other advanced materials have remained in the spotlight of research. Due to its high absorption coefficient, configurable bandgap, long mean free path for carriers, and easy fabrication, the Perovskite solar cell seems to be a potential alternative [1]. The basic crystal structure of perovskite material is ABX_3 , in which A mostly represents organic ions such as methyl ether group (FA) and methylamine group (MA), B represents metal cations (Pb and Sn), and X represents halide ions. The material's properties can be adjusted through dopants or replacement in each element position to tune the bandgap and optimize crystallinity. PSCs typically have a heterojunction structure composed of transparent conductive oxide (TCO) glass substrate, an electron transport layer (ETL), a perovskite film (PSK), and a hole transport layer (HTL), as well as a metallic electrode. The structure of regular PSCs is TCO/HTL/PSK/ETL/Cathode, whereas that of IPSCs exchanges HTL and ETL (TCO/HTL/PSK/ETL/Cathode). When compared to PSCs, IPSCs feature a more straightforward fabrication process, a lower hysteresis, and higher performance when used in tandem configurations [2].

In 2009, Miyasaka identified the applicability of perovskite in sensitized solar cells and fabricate the first PSC with 3.8% PCE [1]. In this work, Miyasaka used $MAPbI_3$ and $MAPbBr_3$ with a liquid electrolyte instead of a heterojunction structure, resulting in exceedingly low efficiency and stability. However, this device successfully achieved photovoltaic conversion of perovskite materials and introduce the two most widely used perovskite materials, pioneering a new field of studies. In 2012,

Park used MAPbI₃ as a light-absorbing layer over a TiO₂ mesoporous layer and incorporated a solid-state HTL material to obtain a PCE of more than 9% [3]. Park's research established the heterojunction structure of solid-state PSCs and created the framework for future advancement. The first IPSC, with ITO/PEDOT:PSS (HTL)/MAPbI₃/PCBM (ETL)/Al configuration, was first proposed in 2013; each layer was superimposed by the spin-coating to achieve a PCE of 3.8% [4]. The studies of HTL materials led the subsequent research in improving the efficiency of the IPSCs. In 2014 IPSC using inorganic NiO_x as the HTL material achieved a PCE of 11% [5]. Based on this study, IPSC with Li dopant in NiO_x to improve the performance of the HTL achieved a PCE of 18% [6]. Degni et al. reached a PCE of 23.7% in 2021 by modifying the HTL/PSK interface as well as the PSK/ETL interface. This is close to the efficiency of the PSC [7]. Either organic or inorganic materials was extensively studied in recent years. In this paper, the recent progress on HTL materials and their interfacial engineering is reviewed. The working mechanism and requirements of HTL materials are first discussed, and the recent progress of organic and inorganic materials is introduced.

2. Hole transport layer

2.1 The requirements for HTL materials

The HTL carried holes generated by perovskite to the TCO. Regarding either regular or inverted structure, HTL materials should have high hole mobility and be capable of blocking electrons to suppress recombination. However, the selection of HTL materials is more restricted due to the inverted structure. Between the common TCO work function (WF) (about -4.5 eV) and the highest occupied molecular orbital (HOMO) of perovskite (MAPbI₃) which is -5.4 eV, there is an energy level gap [2]. Therefore, HTL materials should preferably have an energy level between -5.4 eV and -4.3 eV [2], such that thermal potential loss in the transfer of holes from perovskite film to TCO is minimized. Since the light incidence from the TCO enters the perovskite film via the HTL with the PVK being coated onto the HTL, the HTL materials must have a high optical transmittance for the light within the perovskite absorption spectrum for IPSCs. It should also possess chemical stability so that it would not corrode adjacent layers and good wettability for perovskite solutions to be coated or deposited on it [4]. To fully take advantage of IPSCs' price advantage over conventional PSCs and silicon-based solar cells, it is also preferable that the HTL materials can be manufactured at low-temperature with minimal cost. Many materials have been studied as HTL materials for regular PSCs. but some of them fail to completely meet the above requirements. Therefore, it is necessary to study the HTLs for obtaining efficient and stable IPSCs

2.2 Organic materials

Current HTL materials used in IPSCs can be categorized into organic materials (mostly polymers) and inorganic materials. Meanwhile, HTL-free structure is also achieved by interface engineering. Organic materials used in IPSCs are mostly conductive polymers. They have been widely used in organic photovoltaics and can be easily purchased at a low cost due to their easy fabrication and industrial production on an economic scale. Compared with inorganic materials, polymeric materials obtain several advantages. Polymers possess solution processibility by a structural modification which is essential for industrial large-scale production [6]. Polymers are capable of tuning bandgaps and energy levels through dopants, which can match the HOMO of the perovskite films [7]. They also have high tolerance toward polar solvents due to their relatively large molecule weight [7]. Given the advantages, conductive polymers are extensively studied to enhance device performance.

2.2.1 PEDOT:PSS

Due to its inexpensive cost and high conductivity, PEDOT:PSS is widely applied in organic photovoltaics. Besides, PEDOT:PSS has excellent visible-light transmittance and good conductivity, and it is produced simply using a low-temperature method. Being acidic and hygroscopic, PEDOT:PSS is lack stability and therefore is not an ideal HTL material without modification [2].

Simultaneously, its WF (-4.9 eV) mismatches with the perovskite HOMO (-5.4 eV), resulting in a low V_{oc} , while its deep LUMO (-3.5 eV) results in poor electron blocking [2]. It is anticipated that improvements would lead to pH neutrality, hydrophobicity, a matching energy level, and long-term stability.

Dopants are frequently adopted in PEDOT: PSS solution to obtain desirable properties. Hu et al. doped PEDOT: PSS with sodium citrate (SC), which achieved an optimal PCE of 18.05% (referential 15%) and a V_{oc} of 1.13 V from 1.057 V with 0.08 mol/L dopant concentration through mixing solution [8]. Both the fill factor and current density also significantly increase. Moreover, SC-doped PEDOT: PSS not only tunes the work function (-5.1 eV to -5.32 eV) and pH (2 to 6) but enhances PVK morphology by improving its crystalline growth with suppressed recombination. Li et al. formed a PEDOT: PSS/GQDs composite layer by doping with graphene quantum dots (GQDs). This resulted in a considerable increase in the PCE, which went from the reference value of 12.77% to the champion value of 16.4% [9]. Doping PEDOT: PSS with CsI allowed Jiang et al. to attain a PCE greater than 20%, and they observed no evidence of hysteresis. It has been claimed that making use of alkaline metal salts as additions has the potential to prevent recombination and improve hole extraction capabilities [10]. Doping PEDOT: PSS with KCl, as conducted by Cheng et al., resulted in an increase in PCE from the reference value of 13.79% to 16.24% [11]. The passivation of the interface between HTL and PSK is achieved by the K^+ and Cl^- ion diffusion into perovskite, and KCl-doped PEDOT: PSS is shown to enhance heterojunction crystallization of formed perovskite film [11]. Doping the PEDOT: PSS with Bis(acetylacetonate) dioxomolybdenum(VI) (BADM) allowed Hu et al. to achieve a rise in PCE from 14.26% to 17.11%. This was accomplished by achieving improvements in V_{oc} and Short Circuit Current Density (J_{sc}). Notably, this approach enhances the extensibility of the perovskite film, which eliminates the risk of fractures appearing if the film is twisted [12].

2.2.2 PTAA

PTAA is considered a substitute for PEDOT: PSS because of its ideal electrical properties, chemical neutrality, and hydrophobicity. These characteristics make PTAA more chemically stable over the long term and eliminate corrosion of adjacent layers [13]. Additionally, it achieves a level of energy that is well-matched with perovskite films (-5.2 eV) (-5.4 eV). PTAA also has greater hole mobility ($4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) compared to other organic materials (P3HT: $4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$; spiro-OMeTAD: $2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [14]. However, this hydrophobicity causes the HTL and perovskite layer to have poor wettability, which in turn leads to poor contact between the two. Inadequate contact on the PTAA/PSK interface is harmful to the hole extraction process and results in a significant loss of surface energy during transport. High series resistance is also observed in PTAA [14]. Though, PTAA continues to be the most widely used material for HTL with no convincing alternatives. As is the case with PEDOT: PSS, dopants are often added to improve performance.

In early research, F4-TCNQ was utilized as a dopant to increase conductivity and hole mobility. Through the addition of F4-TCNQ to the PTAA solution, Wang et al. were able to raise the efficiency from 14.8% to 17.5% [14]. Doping with F4-TCNQ results in a reduction in series resistance (9.07 to 6.07 ohm/cm²), an improvement in fill factor (FF) (65.7% to 74%), and an increase in V_{oc} (1.05 V to 1.09 V) without a corresponding reduction in J_{sc} . Organic dopants, on the other hand, increase both the expense and the volatility. As a result, inorganic materials can be considered a possible option for doping. Wang et al. doped PTAA with MoO₃, and as a result, they were able to attain a PCE of more than 20% [15]. MoO₃ is rarely used as a dopant due to its insolubility in commonly used solvents. However, Wang et al. adopted an ammonia solution of MoO₃ and mixed it with the PTAA solution to achieve low-temperature processing.

In recent years, interfacial engineering through surface modification has shown to be an efficient method for creating highly effective PTAA-based IPSCs. Li et al. modified the surface of PTAA with 4,4',4''-(1-hexyl-1H-dithieno [3',2':3,4; 2'',3'':5,6] benzo[1,2-d] imidazole-2,5,8-triyl) tris (N,N-bis(4-methoxyphenyl) aniline) (M2) to form a PTAA/M2/PSK composite layer Xu et al. added an

inorganic potassium fluoride (KF) buffer layer on top of PTAA to manage the surface energy gap, therefore decreasing the HOMO of PTAA from -5.09 eV (without KF) to -5.23 eV (3nm KF) and achieving better PCE (21.51%) and wettability of the perovskite precursor solution [16]. Importantly, after 30 days of exposure to 60% humidity, 90% of the original PCE was still a stable compound [16]. Degani et al. produced the greatest PCE of 23.72% for IPSCs utilizing dual interfacial modification: 2-phenylethylammonium iodide (PEAI) cations were combined into the DMF solution for prewash and into the antisolvent poured into perovskite solution [7]. This approach concurrently boosted FF (85%) and V_{oc} (1.19 V), achieving the champion device performance stated.

2.3 Inorganic materials

An increasing number of inorganic HTL materials have been studied by researchers. Although organic materials have desirable hole transport properties and achieve high efficiency in the laboratory, they cannot be applied to commercial mass production because of their long-term instability, high cost, and complicated preparation. Therefore, researchers have turned to the use of P-type inorganic materials as HTL materials. Many p-type inorganic materials have high transparency, matched energy levels, stability under light, moisture, and heat, and can be used as protective layers for perovskite films [2]. The main research directions are nickel oxide and copper-based compounds.

2.3.1 NiO_x

NiO_x plays a role as a P-type semiconductor for hole transport, and its high light transmission, wide band gap (3.6eV), and extremely close WF (-5.4eV) to HOMO(-5.4eV) of perovskite make it a promising alternative [2]. NiO_x also has desirable thermal stability, affordable prices, and abundant reserves [2]. However, NiO_x still faces many problems: its low intrinsic conductivity can enlarge series resistance, which limits the thickness of NiO_x resulting in poor surface coverage on the ITO substrate; nickel ions on the NiO_x surface can chemically react with the A site atoms of perovskite to form a hole trap and cause recombination loss, which affects the performance of NiO_x-based devices [2].

Metal cations were introduced into NiO_x to increase the conductivity by improving vacancy concentration [2]. Wang et al. revealed that NiO_x doped with lithium and cobalt has superior device performance than single-doped NiO_x HTL, increasing in PCE from 17% to 20.1% [17]. Importantly, this co-doping was performed in a low-temperature solution technique by combining LiNO₃ and FK 209 Co (II) TFSI salt with the NiO_x precursor solution, which was applicable for mass production [17]. Besides, the co-doping of Li and Co also increased the fermi energy from 4.84 eV to 5.27 eV, building a more favorable energy alignment. Lian et al. proposed a dopant-free Ni³⁺-rich NiO_x film fabrication method using UV irradiation at below 82°C, which achieved a PCE of 22.45% [18]. As a high temperature is required for the prevalent fabrication of highly crystallized NiO_x film, this approach significantly reduces the fabrication cost.

To decrease side reactions between NiO_x HTL and the perovskite layer, interfacial engineering was examined in depth. Zhang et al. implanted a trimethylolpropane tris (2-methyl-1-aziridine - propionate) (SaC-100) modifier layer above the perovskite film and reduced the interfacial defects generated by uncoordinated nickel ions to reach a 20% PCE and 1.12 V V_{oc} [19]. Perovskite film formed on top of the SaC-100 layer also showed better crystallinity, and the accelerated decomposition was also blocked by SaC-100 [19]. Li et al. developed a bi-layer structure introducing—4,4"-bis(diphenylamine)-[1,1':3',1"-terphenyl]-5'-carboxylic acid (TPA-BA) in between of perovskite and NiO_x film, which obtained an optimized PCE of 22.25% and high V_{oc} (1.15 V) [20]. The p-type semiconductor layer served to limit the WF of NiO_x and reduce interfacial defects, for which 90% of original PCE was retained after operating for 1000 hours [20].

2.3.2 Cu-based materials

In early studies, copper-based materials were also viewed as ideal non-organic HTL materials, stemming from their lower preparation cost (mostly using low-temperature solutions) and better

conductivity compared to NiO_x -like materials, as well as their excellent light transmission and suitable energy levels [2]. The common Cu-based materials are CuI, CuSCN, and CuO_x [17].

Wang et al. proposed a CuI/CuSCN composite layer as HTL and achieved a PCE of 18.76% largely greater than CuI's PCE (14.53%) and CuSCN's PCE (16.66%) [21]. This composite layer had better film quality without reducing hole conductivity [21]. Later, Ramachandran et al. utilized the electrodeposition method to form a CuI@CuSCN bilayer film and achieved a PCE of 20.35% [21]. Besides, this method creates a larger active cell area and remarkable stability of 1400 h compared with 156 h of the CuI/CuSCN composite layer. Other new materials are also studied. Ye et al. developed a high-performance and stable HTL using CuNbO_x , which obtained a 16.06% PCE with low hysteresis [22]. Yang et al. synthesized CuInS_2 nanocrystals as HTL materials and achieved a PCE of 17.32% with better operational stability than NiO_x [23].

3. Conclusions

In light of the accelerating depletion of fossil fuels, research into high-efficiency, low-cost solar cells are especially vital. IPSCs have become a highly promising growth trend owing to the manufacturing simplicity, low cost of raw ingredients, as well as satisfactory PCE. Although the efficiency of IPSCs has improved significantly in less than a decade, there is still a gap between their efficiency and that of regular PSCs. The significant contribution of HTL in the inverse structure to the advancement of IPSCs cannot be overstated. Currently, the predominant materials employed are mostly organic and inorganic. For organic materials, the most studied and relatively most efficient are PEDOT: PSS and PTAA, while for inorganic materials, NiO_x and Cu-based compounds are used. Devices using organic materials have relatively high PCE, but often do not have long-term chemical stability and low fabrication costs (various dopants need to be added). On the other hand, the stability and relatively low cost of inorganic materials make commercial mass production possible but are limited by their low intrinsic conductivity, which prevents them from achieving very high photovoltaic efficiencies. Despite the extensive research on HTL, researchers have not yet found a perfect solution to achieve high efficiency at low cost and stability to make inverted perovskite cells truly commercially viable. An ideal HTL material should have 1) chemical stability to ensure long-term device operation in various environments 2) HOMO energy level comparable to that of the perovskite layer to prevent possible energy loss at the contact 3) superior hole mobility and conductivity for effective extraction and transport of holes 4) good coverage and wettability to enhance the film formation quality and performance of perovskite. This paper reports the latest research progress on common HTL materials, including the main research directions and the latest improvement ideas, which provide the basis and potential research directions for subsequent research.

References

- [1] Lee, M. M., Teuscher, J., Miyasaka, T., Murakami, T. N., & Snaith, H. J. Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites [J]. *Science*, 2012, 338(6107): 643-647.
- [2] Calió L, Kazim S, Grätzel M, et al. Hole-transport materials for perovskite solar cells [J]. *Angewandte Chemie International Edition*, 2016, 55(47): 14522-14545.
- [3] Kim H S, Lee C R, Im J H, et al. Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9% [J]. *Scientific reports*, 2012, 2(1): 1-7.
- [4] Jeng J Y, Chiang Y F, Lee M H, et al. $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite/fullerene planar-heterojunction hybrid solar cells[J]. *Advanced Materials*, 2013, 25(27): 3727-3732.
- [5] Liu Y, Renna L A, Page Z A, et al. A polymer hole extraction layer for inverted perovskite solar cells from aqueous solutions [J]. *Advanced Energy Materials*, 2016, 6(20): 1600664.
- [6] Nie W, Tsai H, Blancon J C, et al. Critical role of interface and crystallinity on the performance and photostability of perovskite solar cell on nickel oxide [J]. *Advanced Materials*, 2018, 30(5): 1703879.

- [7] Degani M, An Q, Albaladejo-Siguan M, et al. 23.7% Efficient inverted perovskite solar cells by dual interfacial modification[J]. *Science Advances*, 2021, 7(49): eabj7930.
- [8] Hu W, Xu C Y, Niu L B, et al. High open-circuit voltage of 1.134 V for inverted planar perovskite solar cells with sodium citrate-doped PEDOT: PSS as a hole transport layer [J]. *ACS applied materials & interfaces*, 2019, 11(24): 22021-22027.
- [9] Li W, Cheng N, Cao Y, et al. Boost the performance of inverted perovskite solar cells with PEDOT: PSS/graphene quantum dots composite hole transporting layer[J]. *Organic Electronics*, 2020, 78: 105575.
- [10] Jiang K, Wu F, Zhang G, et al. Inverted planar perovskite solar cells based on CsI-doped PEDOT: PSS with efficiency beyond 20% and small energy loss[J]. *Journal of Materials Chemistry A*, 2019, 7(38): 21662-21667.
- [11] Cheng N, Liu Z, Yu Z, et al. High performance inverted perovskite solar cells using PEDOT: PSS/KCl hybrid hole transporting layer[J]. *Organic Electronics*, 2021, 98: 106298.
- [12] Hu Y, Tang Y, Zhang Z, et al. Improving the efficiency of inverted perovskite solar cells by Bis (acetylacetonato) dioxomolybdenum (VI)-doped PEDOT: PSS[J]. *Materials Letters*, 2022, 306: 130911.
- [13] Li Y, Wang B, Liu T, et al. Interfacial Engineering of PTAA/Perovskites for Improved Crystallinity and Hole Extraction in Inverted Perovskite Solar Cells[J]. *ACS Applied Materials & Interfaces*, 2022, 14(2): 3284-3292.
- [14] Liu D, Li Y, Yuan J, et al. Improved performance of inverted planar perovskite solar cells with F4-TCNQ doped PEDOT: PSS hole transport layers[J]. *Journal of Materials Chemistry A*, 2017, 5(12): 5701-5708.
- [15] Wang C, Su Z, Chen L, et al. MoO₃ doped PTAA for high-performance inverted perovskite solar cells[J]. *Applied Surface Science*, 2022, 571: 151301.
- [16] Xu J, Dai J, Dong H, et al. Surface-tension release in PTAA-based inverted perovskite solar cells[J]. *Organic Electronics*, 2022, 100: 106378.
- [17] Wang S, Zhang B, Feng D, et al. Achieving high performance and stable inverted planar perovskite solar cells using lithium and cobalt co-doped nickel oxide as hole transport layers[J]. *Journal of Materials Chemistry C*, 2019, 7(30): 9270-9277.
- [18] Lian Q, Wang P, Wang G, et al. Doping Free and Amorphous NiO_x Film via UV Irradiation for Efficient Inverted Perovskite Solar Cells[J]. *Advanced Science*, 2022, 9: 2201543.
- [19] Zhang J, Long J, Huang Z, et al. Obstructing interfacial reaction between NiO_x and perovskite to enable efficient and stable inverted perovskite solar cells[J]. *Chemical Engineering Journal*, 2021, 426: 131357.
- [20] Li L, Zhang X, Zeng H, et al. Thermally-stable and highly-efficient bi-layered NiO_x-based inverted planar perovskite solar cells by employing a p-type organic semiconductor[J]. *Chemical Engineering Journal*, 2022, 443: 136405.
- [21] Ramachandran K, Jeganathan C, Karuppuchamy S. Electrodeposition of nanostructured bilayer CuI@CuSCN as hole transport material for highly efficient inverted perovskite solar cells[J]. *Journal of Alloys and Compounds*, 2021, 881: 160530.
- [22] Ye X, Wen Z, Zhang R, et al. High-performance and stable inverted perovskite solar cells using low-temperature solution-processed CuNbO_x hole transport layer[J]. *Journal of Power Sources*, 2021, 483: 229194.
- [23] Yang S, Ma W, Zhang Z, et al. Inverted perovskite solar cells based on inorganic hole transport material of CuInS₂ with high efficiency and stability[J]. *Solar Energy*, 2021, 230: 485-491.