

Device Physics of the Carrier Transporting Layer in Planar Perovskite Solar Cells

Xingang Ren, Zi Shuai Wang, and Wallace C. H. Choy*

Perovskite solar cells (PVSCs) have emerged as a promising candidate for addressing the energy crisis due to their rapid efficiency improvement up to 24.2% within 10 years. The defects existing in perovskite film have been found to be as low as 10^{15} cm^{-3} indicating that the bulk nonradiative recombination loss is very small. The major efficiency loss has been attributed to inefficient carrier transportation and collection, particularly at the interfaces of the carrier transport layers (CTLs). Moreover, the mobile ions that can penetrate into or be blocked by the CTLs have been considered to play a significant role in the determination of device efficiency and stability. The further improvement of the PVSC performances relies on interfacial engineering. Meanwhile, it is highly desirable to gain an in-depth physical understanding of interfacial engineering in PVSCs. Herein, the recent works on CTLs in planar PVSCs are reviewed and the device physics for designing high-performance PVSCs is unveiled. This work describes the (1) materials and strategies for efficient CTLs; (2) effects of mobile ions and the influence of CTLs; and (3) theoretical modeling and understanding of PVSCs. This work can, therefore, contribute to designing and improving high-performance PVSCs for future practical commercialized applications.

1. Introduction

The perovskite solar cells (PVSCs) are promising for commercialization in the near future due to the advantages of the solution processing, low cost, and fast improvement of the certified power conversion efficiency (PCE) from 3.8% to 24.2%.^[1] The present concerns regarding the practical applications of PVSCs are their high efficiency and long-term stability. To resolve these issues, the studies of perovskite materials and carrier transporting materials to the electrode are fundamentally important.^[2] In addition, it is essential to unveil the device physics, especially the interfacial properties of PVSCs. The understanding of the loss mechanisms will offer insight and

strategies for efficiency improvement.^[3,4] Currently, it is found that the film quality of the perovskites synthesized by the newly developed approaches is capable of producing an absorption layer delivering the PCE of over 20%. The engineering of the interfacial properties has become a critical issue for the material scientists, engineers, and physicists. The further improvement of PCE requires multidisciplinary collaborative investigations. There are recent reports on the modifications of the commonly used carrier transport materials including the organic materials, inorganic materials, nanocomposites, etc. For the organic materials, 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenyl-amine)-9,9'-spirobifluorene (Spiro-OMeTAD), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), and poly(triarylamine) (PTAA) are typically used to transport holes.^[5–17] The fullerene based materials and their derivatives are also intensively studied as electron trans-

port materials, such as the phenyl- C_{61} -butyric acid methyl ester (PCBM), C_{60} bathocuprione (BCP), etc. Meanwhile, the relatively low-cost nonfullerenes, e.g., 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2',3'-d']-s-indaceno[1,2-b:5,6-b'] dithiophene (ITIC) and their derivatives that possess excellent optical and electrical properties compared with their fullerene counterparts are also promising for highly efficient and stable PVSCs.^[18–29] Regarding the inorganic semiconductor materials, metal oxides possess superior stability and tunable optical and electrical properties compared with the organic semiconductor materials. The various metal oxides such as titanium dioxide (TiO_2),^[13,30–38] zinc oxide (ZnO),^[39,40,38,19,41] and tin oxide (SnO_2)^[42–49] are commonly used as the electron transport layer (ETL), while nickel oxide (NiO_x),^[50–53] copper oxide (Cu_2O),^[54,55] copper (I) thiocyanate (CuSCN),^[16,56,57] copper gallium oxide (CuGaO_2),^[58] and nickel cobalt oxide (NiCoO_x)^[12,59] serve as the hole transport layer (HTL) in the PVSCs.^[60,61] Meanwhile, several theoretical studies based on different approaches to the device models have also been reported, focusing on the underlying physics of the efficiency loss,^[62] hysteresis phenomena,^[63–66] etc., which are substantially affected by the carrier transport layer (CTL) properties. These models enable the analysis of the device performance from the macroscopic circuit aspect^[67] to the microscopic carrier level,^[65] which offer a comprehensive understanding of the device physics of CTLs in PVSCs.

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The judicious selection of the CTLs (i.e., ETL and HTL) enables the improvement of the stability properties of the PVSCs, and enhances the device performance through the suppression of carrier recombination and the elimination of hysteresis issues. In this review, we will first discuss the various carrier transport materials for the interfacial and carrier transport engineering in PVSCs. Second, we will summarize the roles of the mobile ions in determining the current density–voltage (J – V) characteristics in PVSCs and the influences of the carrier transport materials. Third, we will look at the theoretical modeling and understanding of PVSC device physics. Consequently, their work will offer insight into the device physics for the judicious selection of the CTLs and contribute to the future development of PVSCs for their practical applications in photovoltaic systems.

2. Carrier Transporting Layers in Perovskite Solar Cells

The crystallization and film morphology of perovskite will be significantly affected by the underlying CTL, which considerably affect the film quality and highly relate to the PVSC performance.^[11,14,29,59,60,68–71] The CTL properties, e.g., work function, mobility, morphology, and defect, are of critical importance for high-performance PVSCs. Emerging efforts have been carried out to investigate CTL materials for efficient collection of the photogenerated charge carriers. Regarding the instability issue of perovskite materials, it is believed that the judicious selection of the interfacial materials can prevent the material decomposition of perovskite due to moisture and dopant, diffused metal ions from the electrode (e.g., silver, aluminum), etc. The electron and hole transport layers play an equally important role in the extraction of the charge carriers. We will review the recent developments related to these materials, including organic fullerene, fullerene derivatives, nonfullerenes, and inorganic materials of binary and ternary metal oxides.

2.1. Materials and Strategies for Efficient ETL

The semiconductor materials that function as CTL should satisfy the fundamental properties such as the good alignment of the energy level with perovskite, high carrier mobility, decent conductivity, etc. In this section, we will summarize the strategies and employments of some typical semiconductor materials as an efficient ETL.

2.1.1. TiO_x

The energy level of the TiO_2 well matches the conduction band of the perovskite; the well-packed TiO_2 will favor the charge extraction.^[34] To improve the formation of the subsequently deposited perovskite layer as well as the light-trapping properties of the perovskite solar cells, Ho et al. have proposed vertically standing crystalline TiO_2 nanotube arrays through the aqueous TiO_2 sol–gel method on tubular photoresist templates. The uniform and large grain-sized perovskite film can be formed with the help of the TiO_2 nanotube arrays due to the



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facilitated infiltration of the perovskite precursor solution. As shown in **Figure 1a**, the good perovskite/ TiO_2 tube interface not only enhances light-trapping but also allows the efficient electron collection and transport induced by 1D TiO_2 nanotubes; the fabricated PVSCs give an impressive PCE up to 14.13%.^[35] Moon et al. studied the craterlike porous/blocking bilayer TiO_2 ETL by carefully controlling the Ti alkoxide-based sol–gel chemistry. The relatively smooth surface pores with a diameter of 220 nm can function as the light-trapping structure for the reduction of reflection, resulting in the increment of PCE from 13.7% to 16.0%.^[36] With a different approach, the 2D photonic crystal nanodisk pattern formed by the nanosphere lithography method has been incorporated into the TiO_2 ETL (**Figure 1b**), which exhibits a strong forward scattering and contributes to the light harvesting. The TiO_2 with a photonic pattern also

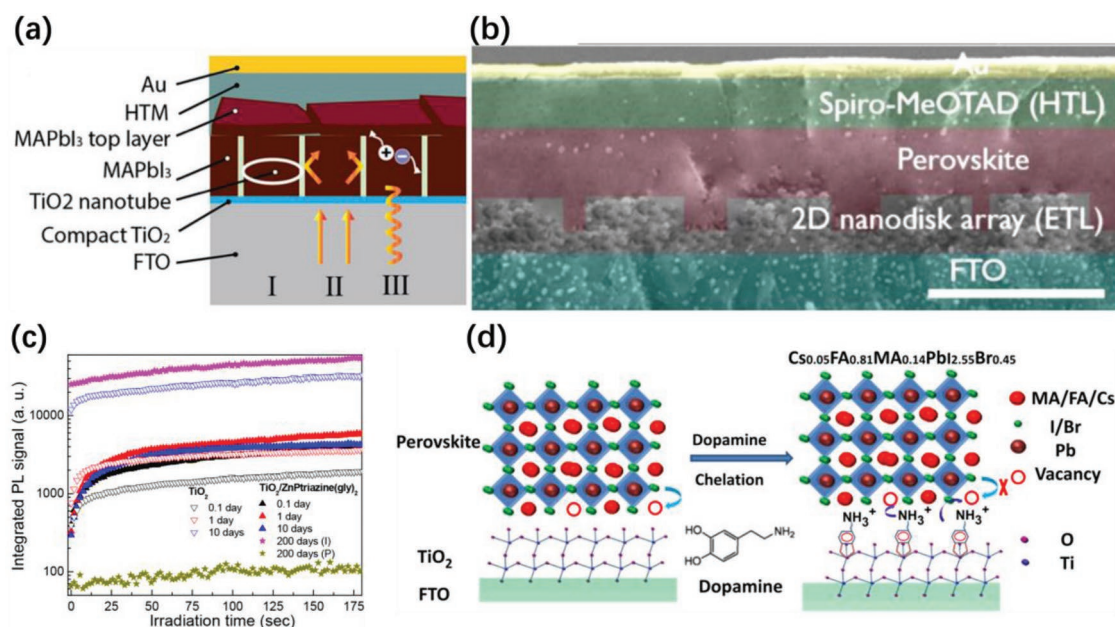


Figure 1. a) Device architecture of the perovskite solar cell. The TiO_2 nanotubes favor the features of (I) high filling rate, (II) light-trapping, and (III) rapid collection and transport of photoexcited electrons. Reproduced with permission.^[35] Copyright 2018, Elsevier. b) The cross-sectional SEM image of the layers in PVSCs, in which the 2D nanodisk array ETL is represented by the gray region. Reproduced with permission.^[37] Copyright 2018, Elsevier. c) PL signal versus time for perovskite films coated on the pristine TiO_2 and porphyrin-modified TiO_2 films aged up to 10 d and the porphyrin-modified TiO_2 film aged for 200 d reveal two regions are monitored either with a negligible or very strong signal. d) Schematic illustration of the passivation effect by the dopamine between the perovskite and TiO_2 interface. Reproduced with permission.^[68] Copyright 2018, American Chemical Society.

reduces the contact resistance and benefits the carrier transport. The optical and the electrical enhancement cooperatively push the PCE to 19%.^[37]

However, the issues of low conductivity and high interfacial defect density suffered by TiO_2 hinder the development of high-performance PVSCs. Therefore, it is essential to improve the synthesis approaches for high film formation quality, or introduce additional materials functioning as doping and passivation agents, etc. Regarding the doping effect, Zhu et al. proposed a facile way to deposit compact TiO_2 (c- TiO_2) film, which is performed by doping the pristine titanium isopropoxide precursor with titanium tetrachloride (TiCl_4). The morphological and structural study clarifies that the doped precursor not only forms a condensed TiO_2 film but also uniformly covers the fluorine-doped tin oxide (FTO) substrate.^[38] In another work, Wang et al. proposed the doping of 1 mol% of Ru into TiO_2 to achieve the characteristics of a suitable band gap, low resistivity, and high carrier density, which improve the charge transport at the compact interface of the TiO_2 , resulting in pushing the PCE from 14.83% to 18.35%.^[13] He et al. have proposed the usage of a one-step spray pyrolysis method to form the Ru-doped TiO_2 films. They found that electrons were rapidly injected from the perovskite layer into ETL due to the good band alignment at the ETL/perovskite interfaces. The results of the impedance spectroscopy further suggest that the adoption of the Ru-doped TiO_2 films can also increase the recombination resistance and decrease the selective contact resistance.^[72]

The surface modifications of the TiO_2 ETL could enable the passivation of the surface defect, improvement of the electron transfer, collection, etc. Huang et al. have investigated the

influence of various dispersants on the TiO_2 electrical properties. They found the pinholes and trap states of the TiO_2 can be effectively reduced by dispersion by the n-pentanol,^[31] leading to the efficient charge transport and reduced recombination. Guo et al. introduced the additional deposition of the subnanometer compact TiO_2 layer to enhance electron extraction and reduce carrier recombination.^[73] Li et al. proposed the phase junction of the anatase/rutile and rutile/anatase TiO_2 , which can efficiently facilitate the separations of the electron–hole pairs and the charge extraction at the interface owing to the reduction of the recombination at the interface of ETL and perovskite by defect passivation.^[72] The incorporation of the other materials allows the additional degree of freedom to optimize the film formation of TiO_2 and subsequent perovskite layer. Grätzel et al. have adopted the CsBr to modify the TiO_2 surface with the strengthened interactions with the perovskite materials.^[74] Fakis et al. have improved the interfacial properties between TiO_2 ETL and $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film by inserting the ultrathin triazine-substituted Zn porphyrin-based film. The capability of electron transferring from perovskite to TiO_2 ETL has been substantially augmented and accelerated due to its chemical modifications. The improvement of the morphology and crystallinity of the perovskite film leads to the significant increment of the short-circuit (SC) current densities and a slight improvement in the fill factor toward the maximum PCE of 16.87% with the stabilized PCE of 14.40%. As shown in Figure 1c, the microphotoluminescence (PL) above 788 nm excitation reveals a clear difference in the PL signal between the TiO_2 -based perovskite film and porphyrin-modified TiO_2 -based perovskite film after the exposure to air for 2 h, 1 d, and 10 d, and the moderate

enhancement of the integrated PL intensity signal of the porphyrin-modified TiO_2 film presents an elevated stability compared with the reference pristine TiO_2 film.^[68] After 200 d, the nonuniform PL signal has been attributed to the decomposition of the perovskite film, where the intact area (denoted as 200 d (I)) shows high PL signal compared with negligible signal for the area degraded into PbI_2 (denoted by 200 d (P)).

2.1.2. SnO_2

Tin dioxide (SnO_2) has high mobility and a wide band gap compared with the TiO_2 .^[43] and allows the usage of a relatively large thickness (≈ 120 nm).^[44] Nazeeruddin et al. proposed the atomic layer deposition method to form the SnO_2 at low temperature, and the careful modulation of the postannealing temperature functioning as the surface passivation of SnO_2 has revealed excellent optical, chemical, and electrical properties, in particular the reduction of the charge recombination at the perovskite/ETL interface leading to high device performance. The further introduction of the bilayer ETL with the configuration of c- TiO_2 and passivated SnO_2 provided better blocking abilities of the minority carrier of the holes, and any efficiency of 20.3% has been achieved.^[49] Wang et al. proposed to use the highly conductive 2D naphthalene diimide-graphene to modify the SnO_2 and form the van der Waals interaction between the surfactant and the perovskite compounds due to the increase in surface hydrophobicity. The enhancement of electron mobility, extraction capability, and the suppressed carrier recombination significantly improve the fill factor to 82% resulting in a device efficiency of 20.02% for $\text{FA}_{0.75}\text{MA}_{0.15}\text{Cs}_{0.1}\text{PbI}_{2.65}\text{Br}_{0.35}$ perovskite.^[45] Xu et al. adopted the $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ solution in a mixed ethanol–water solution with no annealing step in the ultrasound-assisted wet chemistry synthesis approach, and the ultrafine SnO_2 particles with a size of ≈ 2 –5 nm benefit the formation of the ultrasurface on the FTO substrate and deliver a better light transmission compared with the bare FTO substrate.^[42] In addition to the surface modifications, the doping of the SnO_2 such as the Li-doped SnO_2 enables tuning of the conductivity and the conduction band minimum of SnO_2 facilitating the transfer and injection of electrons from the conduction band of the perovskite to the ETL.^[46,47] Correa-Baen et al. studied the effect of the Nb doping on the compositional, structural, morphological, and optical characteristics of the SnO_2 film, which can be deposited by a low-cost, scalable chemical bath deposition method. The PVSCs with the proposed SnO_2 have the lowest series resistance providing a high fill factor.^[48] The above approaches mainly focused on the improvement of the SnO_2 /perovskite interface, which also indicates that the SnO_2 /perovskite interface plays an important role in determining the PVSC performance compared with the SnO_2 /electrode interface.

2.1.3. ZnO

The metal oxide ZnO has an energy level similar to the commonly known TiO_2 but with the high electron mobility and facile synthesis approaches compared with the TiO_2 , which has been widely adopted as the ETL for the perovskite materials. However, the ZnO solution-processed directly on perovskite is limited due

to the reverse decomposition reaction that occurs at the ZnO /perovskite interfaces. This can substantially degrade the charge collection and stability of perovskite solar cells.^[36,38] Jang et al. demonstrated the adoption of the sulfur passivation to reduce the oxygen-deficient defects and surface oxygen-containing groups of ZnO , which not only suppresses the reverse decomposition reaction but also favors perovskite with higher crystallinity and larger grain size. The resultant PCE has been improved to 19.65% simultaneously with long-term stability.^[69] The electron-rich nitrogen-doped ZnO with the one-step deposition approach has been reported to enhance electron transfer owing to improvement in the morphology, conductivity, and optical transmission.^[75]

The incorporation of an additional layer between the ZnO and the perovskite has also been reported to improve the subsequently deposited perovskite layer. Ultrathin Nb_2O_5 has been adopted to improve the interface of ZnO and perovskite, and the perovskite film morphology. The bilayer ETL configurations can not only reduce the surface defects of ZnO but also prevent the decomposition of perovskite due to the direct contact between the perovskite layer and ZnO , as well as the subsequent materials coated on the ZnO .^[59] Yanagi et al. proposed the electrochemical deposition of the high-crystalline ZnO nanorod as a scaffold for the formation of the ZnO - TiO_2 composite, which shows an enlarged contact area between the perovskite and the ETL. The composite ZnO - TiO_2 also favors the reduction of surface defects and the improvement of carrier transport and extraction properties.^[20]

Regarding the interface between the perovskite and the cathode, the energy level alignment between the perovskite and the electrode can be improved with the staircase band alignment. AZO has been inserted between the ZnO and $\text{CH}_3\text{NH}_3\text{PbI}_3$ to form the bilayer ETL configuration. As shown in Figure 2a,b, the weak band bending existing at the interface of the perovskite and the ZnO will hinder the charge separation and result in an increment of the recombination. After the incorporation of the AZO interlayer, the cascade energy level will eliminate the band bending and favor the charge separation process at the ZnO /AZO/perovskite interface compared with the ZnO /perovskite interface, which allows more electrons to be efficiently extracted from the $\text{CH}_3\text{NH}_3\text{PbI}_3$ active layer. The improved carrier extraction and suppressed interface charge carrier recombination ultimately enhanced the PCE from 12.3% to 16.1%.^[41] Another work has proposed the deposition of a thin layer of MgO on the ZnO layer to inhibit the interfacial recombination and subsequently, the further introduction of protonated ethanolamine (EA) to promote efficient electron transport from perovskite to ZnO (Figure 2c). The device efficiency of the proposed ZnO - MgO -EA⁺ has revealed a significant improvement in the open-circuit (OC) voltage (V_{oc}) and short circuit current density (J_{sc}) with less hysteresis effect in the current density–voltage (J – V) curves (Figure 2d). The synergetic effect of MgO and EA not only improves the device efficiency but also prolongs the perovskite stability.^[19]

2.1.4. Organic Materials

The organic semiconductor materials, e.g., the fullerenes based materials, have the highest occupied molecular orbital (HOMO) level that can be well matched between PCBM and the

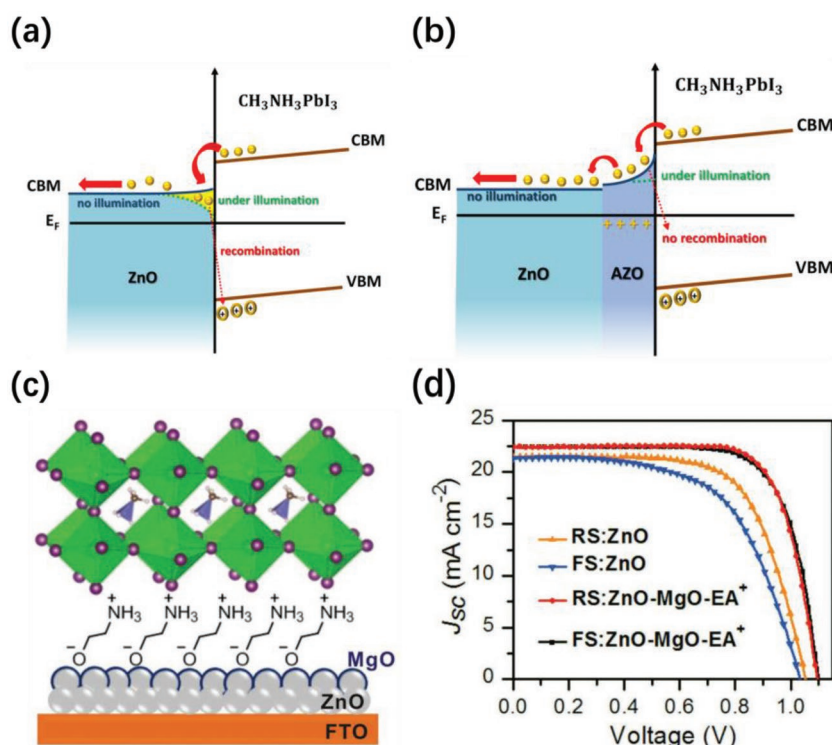


Figure 2. Schematic illustration of field-effect-induced band bending in the heterojunctions of a) ZnO/CH₃NH₃PbI₃ and b) ZnO/AZO/CH₃NH₃PbI₃ without illumination (solid blue line) and with illumination (dashed green line). Reproduced with permission.^[41] Copyright 2017, American Chemical Society. c) Schematic illustration of a planar PVSC device modified with ZnO-MgO-EA⁺. d) The J - V characteristic of the planar PVSC device with the ETL of ZnO-MgO-EA⁺ and ZnO, respectively. Reproduced with permission.^[9] Copyright 2018, Wiley-VCH.

perovskite layer. The typically used fullerene materials of PCBM with rough surfaces can effectively improve the light trapping properties of PVSCs. The interconnected network of the PCBM film itself also favors the electron extraction and elimination of the charge carrier accumulations for a higher V_{oc} .^[21] For the PCBM based ETL, it is essential to deliver a stabilized interface between PCBM and the electrode (e.g., Al, Ag, etc.). Liu et al. reported the insertion of the polyethylenimine ethoxylated (PEIE) in between the PCBM and Al electrode. They found that both the J_{sc} and V_{oc} have been improved. The increment of the J_{sc} has been ascribed to the increased built-in potential and the boosted carrier transport properties by the interface dipole effect, while the increase in the carrier injection barrier due to the decreased defect on the CH₃NH₃PbI_{3-x}Cl_x surface leads to the V_{oc} enhancement.^[22] In a different work, Carnie et al. proposed the interfacial modification with the insertion of the ionic liquid layer of 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄) between PCBM and the Ag cathode (Figure 3a). The experimental measurements of the transient photovoltage and trap density confirm the improvement of the interface contact between PCBM and Ag by the [BMIM]BF₄ (Figure 3b), and the promotion of the electron transport and extraction due to the passivation effect. The resultant PCE of 19.3% and excellent thermal stability have been achieved.^[74] The pillar[5]arene-based small molecule material has been synthesized as the cathode buff layer to modify the interface between PCBM and

Ag, which lowers the work function of the Ag and increases the interface contact area for efficient carrier extraction.^[23]

In addition, the nonfullerene counterparts have the merits of tunable energy level that can be adjusted by various backbones or functional groups. The nonfullerene electron transport materials are capable of overcoming the drawbacks of the traditional fullerene derivatives such as the photochemical stability, energy level variability, production cost, etc.^[19] Furthermore, the adoption of the nonfullerene ITIC as the ETL has shown a PCE comparable to that of the PCBM based device.^[24,25] The other fullerene and nonfullerene based organic semiconductor materials, e.g., NDI-ID (N,N'-Bis(1-indanyl)naphthalene-1,4,5,8-tetracarboxylic diimide) and the derivative^[27,76] the fullerene derivatives C₆₀MC₁₂ (C₆₀-fused N-methylpyrrolidinemetadodecyl phenyl),^[28] CPTA-E (C₆₀ pyrrolidine tris-acid ethyl ester)^[29] have also been reported to achieve high device performance of ≈20% for various types of perovskite materials. Meanwhile, Lin et al. demonstrated the advantages and effectiveness of the bifacial modifications of the two CTLs in PVSCs. For the HTL, the self-assembled dye molecule monolayer has been adopted to passivate the NiO_x, resulting in a better energy level alignment, reduction of surface trap states, and improvement of the crystallinity of the perovskite layer. For the

ETL, the composite layer of the BaSnO₃ nanoparticles (NPs) and PCBM has been used to elevate the electron transport and device stability. The PCE has been enhanced from 14.0% to 16.2% due to the synergetic effect of the bifacial interface modifications.^[70]

2.1.5. Bilayer and ETL Free

The ETL with bilayer configuration has also been widely studied, which demonstrated several advantages including the efficient transport and collection of the free charge carriers as well as long-term stability. There are several types of the bilayer-configured ETL architectures including the ZnO/C₆₀,^[13] ZnO/AZO,^[77] SnO₂/ZnO,^[78] NiO_x/ZnO,^[79] MgO/SnO₂,^[80] etc. Choy et al. have demonstrated a thick TiO₂ backbone film directly forming on top of a perovskite film through a room temperature solution process. As the schematic illustration shown in Figure 3c, the strategy of decorating the TiO₂ film with fullerene can fill the voids that normally lead to the trap passivation. The fullerene-decorated TiO₂ ETL in inverted PVSCs has a smooth morphology for the subsequent deposition of silver as the electrode (Figure 3d), which can suppress Shockley-Read-Hall recombination and ion diffusion of the fullerene-decorated TiO₂ ETL. The results showed a stabilized efficiency of 20% and shelf-life stability over 98% of initial efficiency after aging under ambient conditions

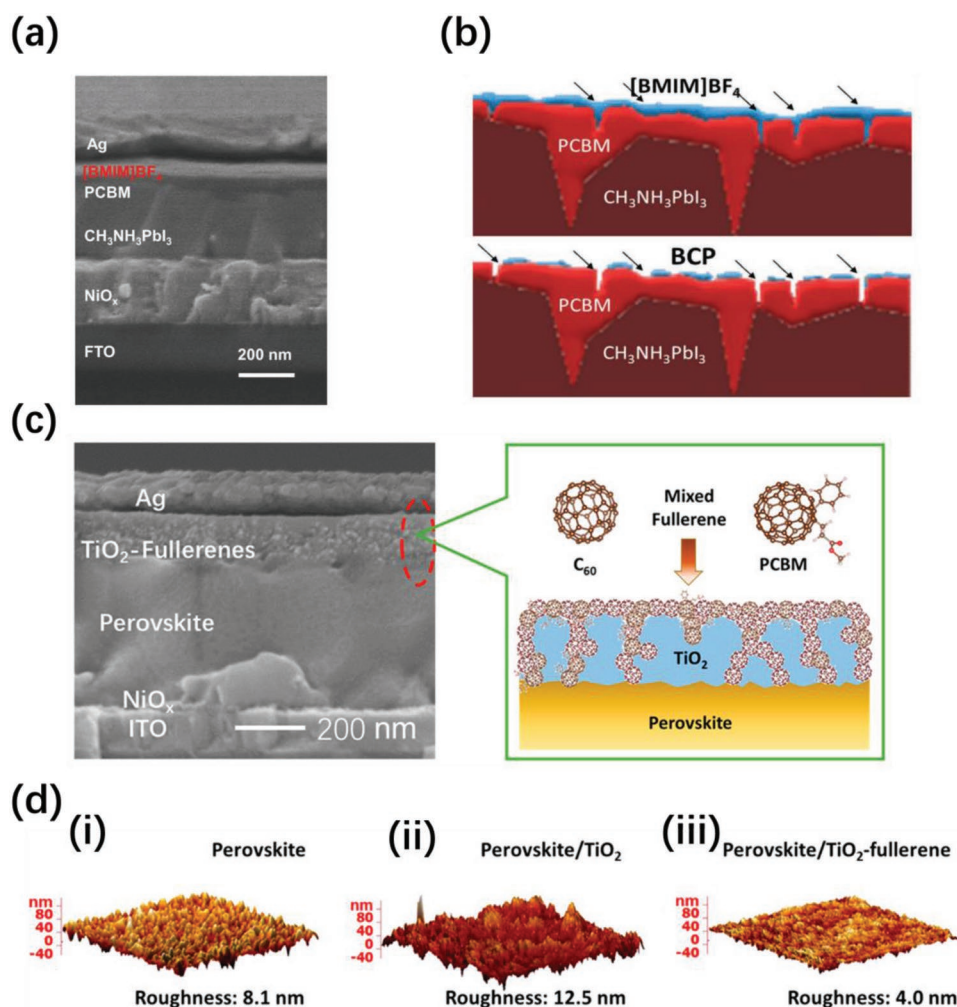


Figure 3. a) The cross-sectional SEM image of the [BMIM]BF₄-based PSCs. b) A schematic of the different passivation effects by BCP and [BMIM]BF₄. Reproduced with permission.^[74] Copyright 2018, Wiley-VCH. c) High-resolution cross-sectional SEM image and the relevant schematic diagram of a complete solar cell with fullerene-decorated TiO₂ as the top ETL. d) 3D AFM images of (i) perovskite film, (ii) TiO₂ film on perovskite, and (iii) fullerene-decorated TiO₂ film on perovskite. Reproduced with permission.^[81] Copyright 2018, American Chemical Society.

for ≈16 months.^[81] Brown et al.^[80] reported a bilayer ETL configuration based on a thin layer of MgO between the SnO₂ and perovskite. Benefitting from the more uniform films and reduction of interfacial recombination, MAPbI₃ based PVSCs with this configuration achieved PCE 25% for 200 lx indoor illumination and 26.9% for 400 lx, which showed ≈20% improvement compared with the control devices without the thin MgO layer.

Different from the various strategies to engineer the ETL, the ETL-free perovskite solar cells with judicious interfacial engineering also reveal high efficiency and decent stability.^[82] The insertion of the insulated interlayer of BCP between the perovskite absorber and the FTO electrode improves the device efficiency from several different aspects: 1) a pronounced enhancement of charge transfer efficiency between the perovskite and the electrode from 60.98% to 74.18%, by modulation doping and band bending effects; 2) suppressed leakage current due to the insulation property; 3) increased conductivity of the FTO electrode, proved by the current mapping image; 4) modification of the perovskite crystal size; and 5) prevention of exciton quenching at the perovskite/FTO interface. Moreover,

the BCP-based ETL-free devices retained 92.2% of their initial performance after 450 h of continuous AM 1.5 soaking.^[71]

2.1.6. Other Materials

In addition to the abovementioned metal oxides as ETL, other types of semiconductor materials have also been proposed as efficient ETLs for high-performance PVSCs. Lee et al. reported the amorphous Zn₂SnO₄ (am-ZTO) films, which have high electron mobility, excellent surface uniformity, and fewer charge traps. Enhanced carrier extraction and reduced recombination can be achieved by the careful control of the stoichiometric ratio of Zn and Sn, which also shows an improved stability and reduced hysteresis.^[26] Li et al. proposed the adoption of the 2D transition metal dichalcogenide TiS₂ as the ETL, for which the average PCE maintains 95% of its initial value after 816 h of storage indicating extremely long-term stability.^[83] Chu et al. reported the insertion of the bilayer PCBM/[EMIM]PF₆ between Nb₂O₅ and perovskite, in which the PCBM can

improve the electron extraction ability by the surface passivation of Nb_2O_5 and the [EMIM]PF₆ can improve the hydrophilicity of PCBM and protect the dissolution of PCBM in the subsequent deposition of the perovskite layer.^[84] The adoption of various ETL materials in perovskite solar cells and their corresponding efficiencies are summarized in Table 1.

2.2. Materials and Strategies for Engineering Efficient HTL

With the same approach for the ETLs, there are various reports regarding engineering of efficient HTLs including the modification of the state-of-the-art materials such as PEDOT:PSS, Spiro-OMeTAD, and NiO_x , and the synthesis of new material such as ternary metal oxide, organic materials, etc. Here, we will focus on the summaries of recent works from the aspects of material selection and device physics of interfacial engineering.

2.2.1. PEDOT:PSS

The advantages of transparency, conductivity, and excellent film morphology make PEDOT a good candidate for an HTL for perovskite solar cells. PEDOT with an ultrathin thickness has been reported to significantly enhance the PCE to 19.3% from 16.9% of the control device with thick PEDOT.^[12] There are various works contributing to the modification of the electrical properties of PEDOT:PSS such as the conductivity, blocking ability of minority carriers, charge transport, etc. Su et al. showed that the dopamine (DA) modified PEDOT:PSS has a stronger charge extraction capability than the control pristine PEDOT:PSS. The results of the photoluminescence and electrochemical impedance spectroscopy reveal that the dopamine-modified PEDOT:PSS has the properties of efficient hole transport and electron blocking.^[13] The blend of the additive poly(2ethyl-2-oxazoline) (PEOz) with PEDOT:PSS can increase the work function of HTL favoring hole transport, and enlarge the grain size of the perovskite for device efficiency improvement.^[14] Yu et al. studied the insertion of ammonium metatungstate hydrate into PEDOT:PSS, which modifies the surface properties yielding the subsequent deposition of perovskite with large average grain size and a smooth and dense film.^[29] Huang et al. reported that the DA semiquinone radical-modified PEDOT:PSS as HTL with a radical content can deliver a greater charge extraction capability from perovskite to HTL. In addition, other advantages such as an increment in the work function, improvement of film crystallinity, interaction with the undercoordinated Pb atoms on the perovskite crystal by the amino and hydroxyl groups in DA, and reduction of carrier recombination rate have also been observed with the DA doping.^[11]

2.2.2. Spiro-OMeTAD

The usage of Spiro-OMeTAD as an HTL serves as a milestone in the development of high-performance perovskite solar cells due to its facile implementation.^[5] The issues of cost-performance, stability, and degradation remain to be resolved. Cheng et al.

proposed tetrabutylammonium (TBA) salts for the organic hole transport materials of the Spiro-OMeTAD. The anions in the TBA salts are of importance in the hole conductivity, smoothness of the HTM layer, hysteresis, and stability of the devices.^[6] The incorporation of the phenyl-thiophene units in the 2D and low-cost p-conjugated molecule OMe-TATPyr not only favors the carrier transport through enhanced charge delocalization and intermolecular stacking but also contributes to the defect passivation via Pb-S interaction.^[7] Ahmad et al. introduced the insertion of BMPyTFSI in Spiro-OMeTAD HTL as both the p-type dopant and an additive. The conductivity of Spiro-OMeTAD has been improved by two orders of magnitude due to its functionality as the dopant. The role of the additive has reduced the carrier recombination and facilitated the formation of a pinhole-free HTL surface.^[8] In addition, the new Spiro-OMeTAD derivatives as the hole-selective materials have also been widely reported.^[9,10]

2.2.3. PTAA

The polymeric properties of the PTAA as an HTL have also been studied in detail. Examinations of the correlation between the molecular weight and polydispersity index with the solubility, film formation, rheological properties, and carrier mobility is important in the fabrication of uniform perovskite film for large area device.^[16] Jia et al. employed a fluorine-containing hydrophobic Lewis acid dopant (LAD) as an effective dopant for PTAA. In this case, the nonextrinsic Li^+ -ion migration and trap states at the perovskite surface have been passivated by the LAD, which results in an excellent fill factor of 0.81 and as high as 19.01% and prolonged stability up to 70 d while maintaining the initial efficiency of 78%.^[17]

2.2.4. NiO_x

NiO_x has been widely studied due to the degree of tunability of its optical and electrical properties for various compositional perovskites. The implementations of the mesoporous NiO_x scaffold^[9] and nanoporous NiO_x ^[15] have reported to address the underlying contact issues between NiO_x and perovskite film. Choy et al. demonstrated a flawless and surface-nanostructured NiO_x film with a controllable room-temperature solution process.^[51] As shown in Figure 4a,b, the proposed NiO_x has a deeper valence band of -5.4 eV that is much closer to the valence band of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (-5.47 eV) and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (5.58 eV) compared with the conventional HTL PEDOT:PSS (VB = -5.1 eV), resulting in an ohmic contact. In particular, the conduction band of NiO_x (-1.8 eV) is dramatically closer to the vacuum level compared with that of perovskite, indicating the efficient inhibition of the electron leakage of NiO_x . In addition, the surface-nanostructured NiO_x film contributes to the reduction of the interfacial recombination and monomolecular nonradiative recombination in perovskite solar cells. Hole extraction has been essentially improved due to the formation of the large interfacial area of the NiO_x film/perovskite layer, resulting in a PCE of 16.7% with no obvious hysteresis (Figure 4c).

Table 1. Summarization of the various electron transport layer for perovskite solar cells.

Electron transport material	Device structure	Physical	PCE	Ref.
TiO ₂	Ag/Spiro-MeOTAD/MAPbI ₃ /Porphyrin/TiO ₂ /FTO	Zn porphyrin between TiO ₂ and the CH ₃ NH ₃ PbI ₃ , improved electron transfer toward TiO ₂ and augmented the perovskite morphology	16.87%	[68]
TiO ₂	Au/Spiro-MeOTAD/perovskite/TiO ₂ /FTO	Different dispersants	18.16%	[31]
TiO ₂ phase junction	Ag/Spiro-MeOTAD/perovskite/TiO ₂ -phase junction/FTO	Effective in separating electron-hole pairs at the interface	15.34%	[72]
Vertical TiO ₂ nanotube arrays	Au/Spiro-MeOTAD/perovskite/vertical TiO ₂ /FTO	Good interfacial contact at perovskite/TiO ₂ tube interface, enhance light trapping	14.13%	[35]
2D photonic crystal nanodisk array	Au/Spiro-OMeTAD/perovskite/2D nanodisk array/FTO	Optimized ND arrays exhibit strong forward scattering and optical confinement effects, greatly enhancing light harvesting in the perovskite layer	19%	[37]
TiO ₂ surface by CsBr	Cs-doped mp-TiO ₂ and quadruple-cation (Rb/Cs/FA/MA)	Large contact area, strengthens the interaction of TiO ₂ and perovskite	21%	[74]
Ru-doped TiO ₂	Au/Spiro-MeOTAD/perovskite/Ru-doped TiO ₂ /FTO	Improved conductivity, increase in recombination resistance	15.7%	[72]
Ru-TiO ₂	FTO/Ru-TiO ₂ /Meso-TiO ₂ /MAPbI ₃ /Spiro-OMeTAD/Au	Suitable band gap, low resistivity, and high carrier density	18.35%	[13]
Fullerenes modified TiO ₂	Ag/MoO ₃ /SpiroOMeTAD/CH ₃ NH ₃ PbI ₃ /bis-PCBM/TiO ₂	Exhibit excellent hole mobility and desired surface energy to the perovskite uplayer	20.14%	[94]
ETL-free with insulator BCP	Ag/SpiroOMeTAD/perovskite/BCP/FTO	Modified FTO surface work function, and enhance the charge transfer between FTO and perovskite	19.07%	[71]
SnO ₂	FTO/ALD SnO ₂ /perovskite/poly triarylamine (PTAA)/gold layers	Surface passivation of SnO ₂ is essential to reduce charge recombination at the perovskite and ETL interface	20%	[49]
SnO ₂	Au/Spiro-MeOTA/perovskite/SnO ₂ /FTO	Ultrasonic-assisted wet chemistry synthesis of ultrafine SnO ₂ nanoparticles	16.56%	[42]
Nb-doped SnO ₂	FTO-coated glass/SnO ₂ /perovskite/Spiro-OMeTAD/Au	Structural, compositional, morphological, and optical characteristics	20.5%	[48]
SnO ₂ with 2D naphthalene diimidegraphene	Au/Spiro-OMeTAD/perovskite/SnO ₂ NDI/ITO	Increase surface hydrophobicity and form van der Waals interaction between the surfactant and perovskite	20.2%	[45]
ZnO	Au/Spiro-MeOTAD/MAPbI ₃ /Nb ₂ O ₅ /ZnO/FTO	Ultrathin Nb ₂ O ₅ passivation layer effectively prevents direct contact between the ZnO and perovskite and prevents the decomposition of perovskite	14.57%	[59]
ZnO/AZO bilayer	FTO/ZnO/AZO/CH ₃ NH ₃ PbI ₃ /Spiro-OMeTAD/MoO ₃ /Ag	Modified interface in the ETL with staircase band alignment of ZnO/AZO/CH ₃ NH ₃ PbI ₃	16.1%	[41]
ZnO-MgO	SpiroOMeTAD/CH ₃ NH ₃ PbI ₃ /ZnO-MgO/FTO	Inhibits the interfacial charge recombination	21.1%	[19]
Nitrogen-doped ZnO	FTO/blocking layer/n-ZnO/perovskite/Spiro-OMeTAD/Ag	Better morphology, conductivity, and optical transmittance	14.40%	[75]
SnO ₂ /ZnO bilayer	ITO/(SnO ₂ /ZnO)/CsPbI ₂ Br/SpiroOMeTAD/MoO ₃ /Ag	Cascade energy level alignment between the perovskite and SnO ₂ /ZnO bilayered ETL	14.6%	[78]
ZnO/C ₆₀ bilayer	FTO/NiO _x /CsPbI ₂ Br/ZnO/C ₆₀ /Ag	High carrier extraction efficiency and low leakage loss	13.3%	[13]
Sulf passivated ZnO	Au/HTM/CH ₃ NH ₃ PbI ₃ /ZnO-S/ITO	Reduces the oxygen-deficient defects and surface oxygen-containing groups	19.65%	[69]
PCBM/ZnO	ITO/PEDOT:PSS/CH ₃ NH ₃ PbI ₃ /PCBM/Al	Electron selective layer between PCBM and back contact	12.01%	[77]
NDI-ID	ITO/PEDOT:PSS/FAPbI _{3-x} Br _x /NDI-ID/Al	Alicyclic and aromatic characteristics	20.2%	[76]

Table 1. Continued.

Electron transport material	Device structure	Physical	PCE	Ref.
FA ²⁺ -PDI ₂	Ag/FA ²⁺ -PDI ₂ /perovskite/NiO/FTO	Overcome the drawbacks of the traditional fullerene derivatives	17.0%	[19]
PCBM/PEIE	ITO/PEDOT:PSS/CH ₃ NH ₃ PbI _{3-x} Cl _x /PCBM/PEIE/Al	Reduce the hysteresis effect	14.46%	[22]
PCBM/[BMIM]	FTO/NiO _x /PCBM/[BMIM]BF ₄ /Ag	[BMIM]BF ₄ paves the interface contact between PCBM and electrode and facilitates the electron transport	19.30%	[74]
CPTA-E	Al/CPTA-E/CH ₃ NH ₃ PbI ₃ /P3CH/ITO	CPTA-E ETL has a preferable charge quenching effect	17.44%	[29]
NiO _x -ZnO/PCBM	Al/PCBM/ZnO/perovskite/NiO _x /ITO	Ultrasmooth and pinhole-free perovskite	18.6%	[79]
BSO/PCBM	Ag/BSO/PCBM/perovskite/NiO/FTO	Superior electron transport properties and excellent device stability	16.2%	[70]
Zn ₂ SnO ₄ (Am-ZTO)	Spiro/perovskite/Am-ZTO/FTO	Extreme surface uniformity, high electron mobility, and fewer charge traps	20.02%	[26]
C ₃ between PCBM and Ag	Ag/C ₃ CBL/PCBM/perovskite/HTL/FTO	C ₃ modify the PCBM/Ag interface, enhance the diode properties of devices, and facilitate electron transport	17.42%	[23]
Deposited Nb ₂ O ₅	Ag/SpiroOMeTAD/perovskite/Nb ₂ O ₅ /FTO	Excellent optical transmittance, and similar Femi level of TiO ₂	16.2%	[84]
2D TiS ₂	Ag/SpiroOMeTAD/perovskite/2D TiS ₂ /ITO	High stability	18.79%	[83]

In addition to the decent properties of the NiO_x, there are still some detrimental electrical properties, e.g., the high surface trap density and low electrical conductivity, which could restrain the widespread applications of the pristine NiO_x film in solar cell application. Several works have reported the effectiveness of doping for elevating the NiO_x electrical properties. Hagfeldt et al. investigated Cs-incorporated NiO_x and found the suppressed generation of a Ni phase in the NiO_x layer after the employment of the cesium. The increment of the recombination resistance by three-fold and efficient hole separation cooperatively contribute to the resultant PCE of 17.2%.^[85] The Zn-doped NiO_x and Cu-doped NiO_x have also been reported to favor the highly crystalline oxide materials.^[86,87] Hu et al. examined the concentrations of cobalt (Co)-doped NiO_x in adjusting the work function and electrical conductivity (Figure 4d). They further inserted an insulating polymer layer for the passivation of the interfacial recombination center and the suppression of current leakage at the perovskite/HTL interface. The boosted V_{oc} of 40 mV consequently enhances the average PCE up to 20.3% (Figure 4e). The bias-dependent PL was performed with the applied voltage varying from J_{sc} to V_{oc} . As shown in Figure 4f, the Co-doped NiO_x can suppress the radiative recombination by the passivation of the grain boundary defects. The increment in the ΔPL of Co-doped NiO_x-based device indicates that the doped HTL can reduce charge recombination for the improvement of device performance.^[12]

2.2.5. Double-Layer Configuration

The double-layer configuration of the HTL has offered an additional degree of freedom to manipulate the HTL optical and electrical properties.^[88] For instance, the reduced graphene

oxide (r-GO)/copper (I) thiocyanate (CuSCN) has served as an efficient bilayer HTL, in which the thickness of the CuSCN interlayer at the r-GO/MAPbI₃ interface play an important role in enhancing the stability and photovoltaic performance. As shown in Figure 5a, the well-matched energy level favors the inhibition of recombination at the MAPbI₃ interface with faster hole extraction. The stability of the perovskite solar cells has also been substantially improved with the bilayered HTL configurations (Figure 5b).^[16]

In another work, the incorporation of Au and MoO_x NPs in graphene oxide (GO) can increase the work function of GO; the downshifts of work functions lead to a decreased level of potential energy and hence increased V_{oc} of the PVSC devices.^[89] Diau et al. provided us the underlying process of hole transfer from the GO, NPs and to the electrode for an understanding of the charge recombination in the perovskite/GO-NP interface. As the illustration shows in Figure 5c, the enhanced hole extractions in the hybrid GO/NP systems is because of the p-doping effect of both Au NP and MoO_x NP. The Au NP on the surface of GO benefits rapid extraction of holes, but the extracted holes could also be equilibrated inside the Au NP, with the subsequent transfer of holes to the ITO hence becoming slow and resulting in a decreased J_{sc} . In contrast, in the case of the GO-MoO_x film, the hole extraction from perovskite to GO-MoO_x was rapid due to the p-doping and delocalization of the extracted holes, therefore the holes can be efficiently transferred to the ITO.

2.2.6. New Organic Materials

The development of various kinds of small-molecule and polymeric HTLs is promising as potential alternatives to the

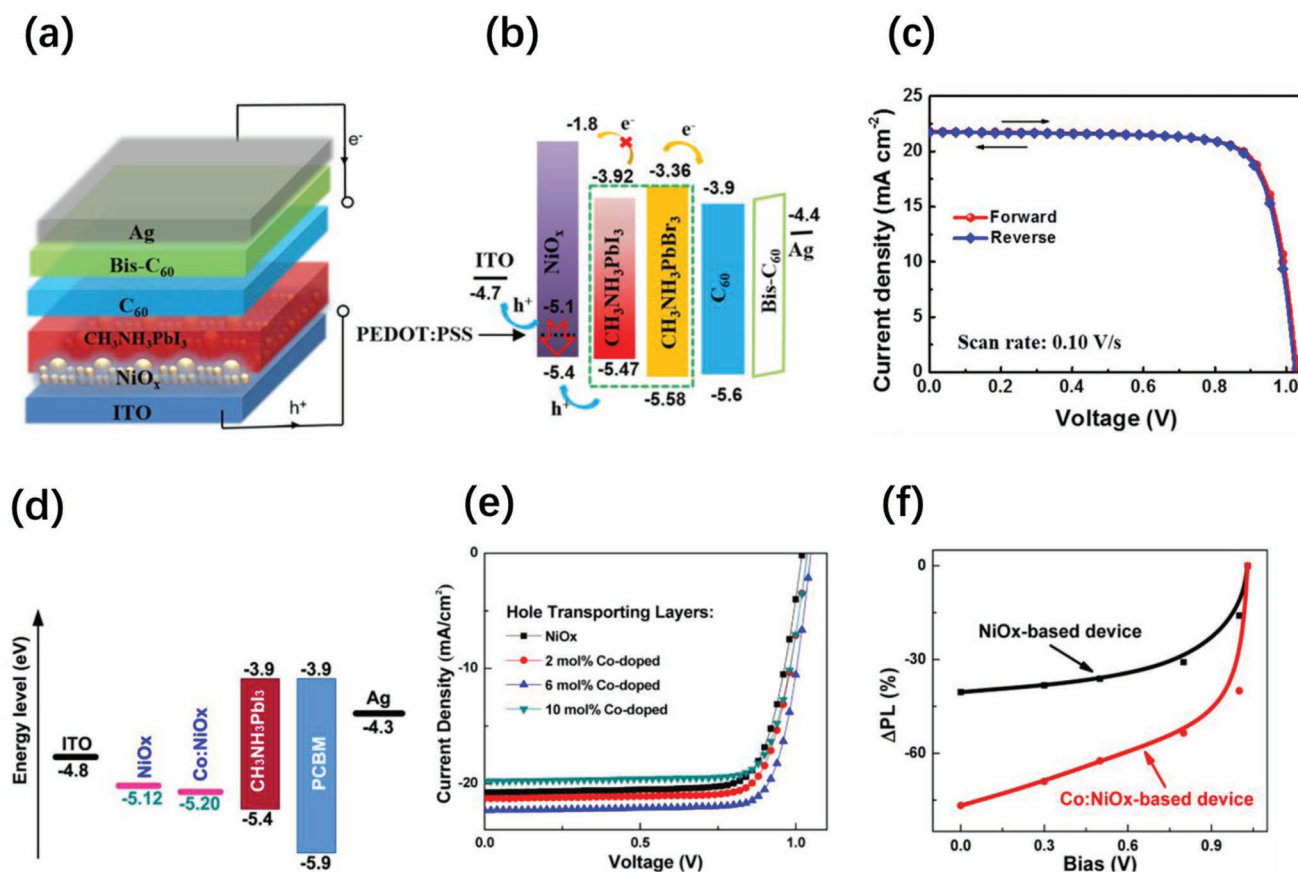


Figure 4. a) Device structure of PVSCs in this study and b) corresponding energy band diagram relative to the vacuum level. c) J - V curves for the NiO_x -based PVSCs measured under different scan directions. Reproduced with permission.^[51] Copyright 2016, American Chemical Society. d) Energy alignment diagram. e) Current density-voltage (J - V) characteristics of the PVSCs with different ratios of Co in NiO_x under standard test conditions (AM 1.5G, 100 mW cm^{-2}). f) Steady-state PL spectra measured for NiO_x and Co-doped-based device from short-circuit condition to open-circuit condition. Reproduced with permission.^[12] Copyright 2018, American Chemical Society.

high-cost Spiro-OMeTAD, e.g., the electron-rich molecule H101 (3,4-ethylenedioxythiophene),^[90] the star-shaped thiophene-containing HTL based on fused tetrathienoanthracene and nonfused tetrathienylbenzene cores,^[91] nonspiro fluorine-based V1050 and V1061,^[92] etc. The dimeric porphyrin named WT3 exhibits a proper HOMO level, high hole mobility, and efficient charge extraction for perovskite solar cells leading to a PCE of 19.44%.^[93] The use of a novel small molecule TPE (tetrakis(tri-phenylamine), prepared by a facile synthetic route as a superior dopant-free HTL, can serve as an excellent HTL due to the suitable band alignment and efficient hole extraction/collection.^[94] The report of the BDPSOs (disodium benzodipyrrole sulfonate) includes its functions as a neutral, nonhygroscopic, dopant-free HTL for lead perovskite (MAPbI_3) solar cells. The tunable orbital level and controllable solubility push the PCE to 17.2%.^[95] Two novel H-shaped HTLs, G1 and G2 based on the dispiro-rings as the cores, are synthesized. The resulting high PCE of 20.2% has been ascribed to good film formation, better interactions with perovskite, slightly deeper HOMO, higher mobility, and more efficient charge transfer.^[96] The additional management of the new organic material could also deliver better electrical performance. For example, a small amount of Li-TFSI was added into the P3HT HTL to improve the carrier

density and achieve a high PCE of 17.55%.^[95] The introduction of a thin interlayer of PVP (poly(4-vinylpyridine)) between the perovskite and the hole transport layer reveals the suppression of the nonradiative recombination, leading to a high V_{oc} of 1.20 V with a stabilized efficiency of 20.7% for the best devices. This improvement has been attributed to the passivation of the trap states on the perovskite surface and possibly at the interface with the HTL.^[97]

2.2.7. Inorganic Materials

The organic HTLs, e.g., molecular Spiro-MeOTAD, polymeric PTAA, etc. have poor stability and the issue of large-scale commercial applications. Inorganic HTLs have the merits of the long-term stability and efficiency comparable to the organic HTL-based perovskite solar cells.^[12] The Au-doped CuPc (phthalocyanine) film reduces shunts and interface recombination toward the efficiency of 20% with negligible hysteresis.^[91,98] The other inorganic hole transport materials, e.g., CuSCN ,^[56,57] CuGaO_2 ,^[58] and sputtered nitrogen-doped Cu_2O ,^[54,55] have also revealed high device performance and long-term stability. Kymakis et al. reported the introduction of solution-processed

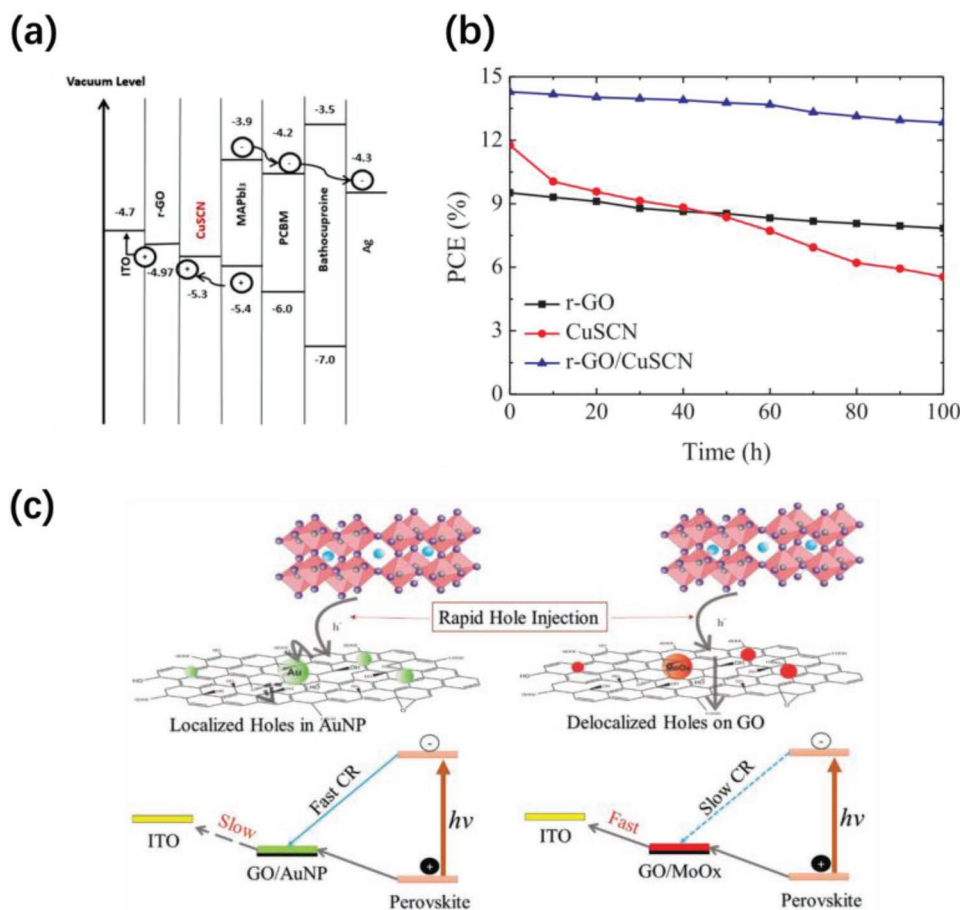


Figure 5. a) Energy level diagram. b) Light soaking stability of the unsealed PVSCs fabricated by r-GO, CuSCN, and r-GO/CuSCN HTLs. Reproduced with permission.^[16] Copyright 2018, Elsevier. c) Schematic representation of the mechanism of hole transport in GO-AuNP and GO-MoOx devices. Reproduced with permission.^[89] Copyright 2018, Wiley-VCH.

MoS₂ flakes between the PTAA HTL and MAPbI₃ film, which delivers a PCE of 17% with ultrastable perovskite solar cells stressed under ambient conditions with working conditions at the continuous maximum power point. As shown in **Figure 6**, these represent the current state-of-the-art in terms

of lifetime, retaining 80% of their initial performance after 568 h of a continuous stress test, thus near the industrial stability standards.^[99]

Choy et al. proposed a novel strategy to synthesize ultrasmall ternary oxide NPs of NiCo₂O₄, based on controllable

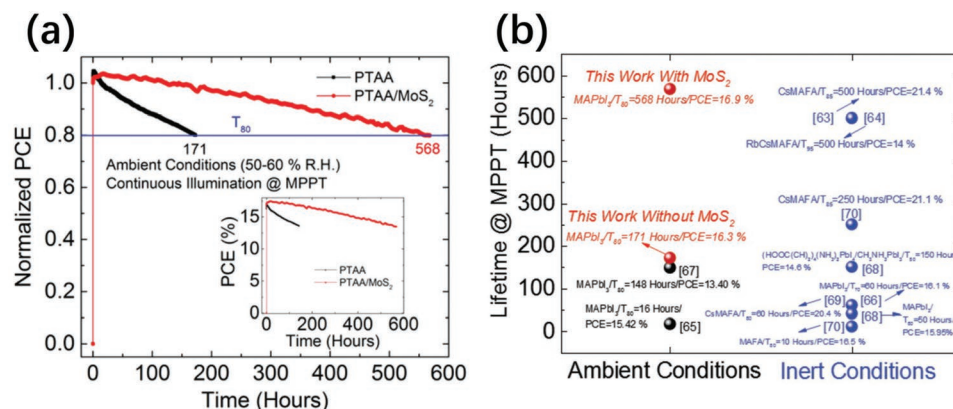


Figure 6. Long-term stability of encapsulated PVSCs and state-of-the-art lifetimes reported to date. a) The lifetime of PVSC PCE under continuous illumination at the MPP tracking of devices with (red) and without MoS₂ (black) in ambient conditions. Inset: Actual MPP values obtained for both devices. b) State-of-the-art lifetimes reported in continuous device operation in the above-mentioned conditions of high-efficiency PVSCs in both ambient (black) and inert conditions (blue). Reproduced with permission.^[99] Copyright 2018, Wiley-VCH.

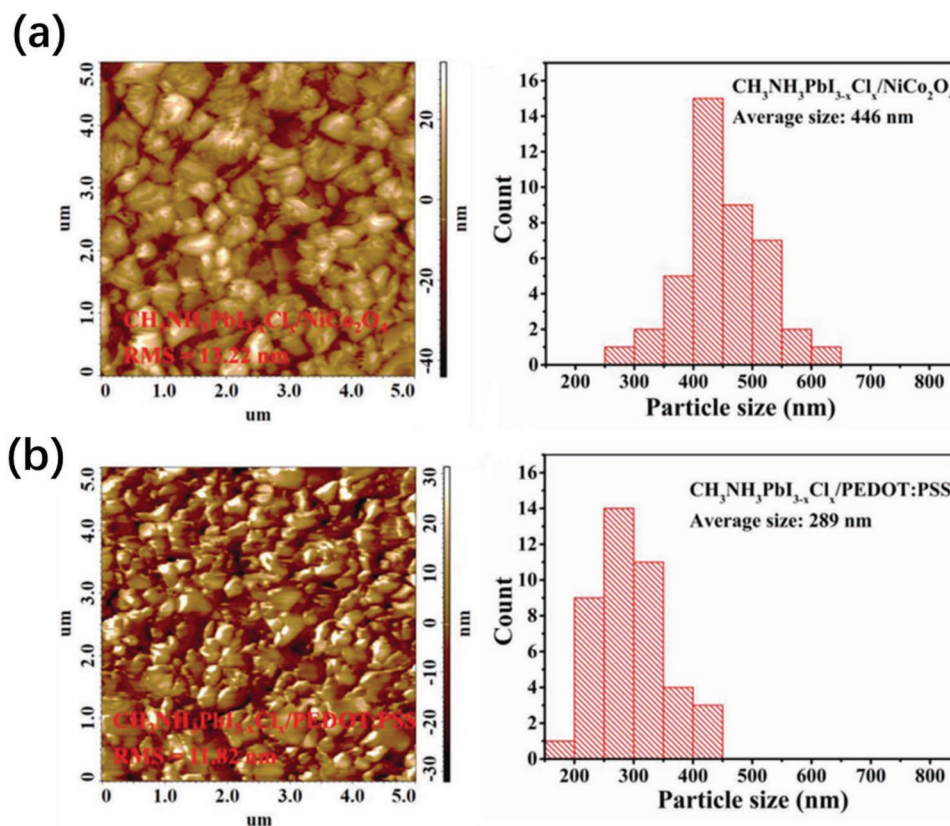


Figure 7. AFM images of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ a) on NiCo_2O_4 and b) on PEDOT:PSS and size distribution histogram of the perovskites. Reproduced with permission.^[59] Copyright 2018, Wiley-VCH.

deamination of Co-NH₃ complexes in a system containing Ni(OH)₂. As shown in Figure 7, through this method, the ultrasmall (5 nm on average) and well-dispersed NiCo_2O_4 NPs without exotic ligands are made to form uniform and pin-hole free films. The tightly covered NiCo_2O_4 films also benefit the formation of large-grain-size perovskite and thus reduce film defects. The PCE of 18.23% and promising stability (maintaining 90% PCE after 500 h light soaking) have been achieved.^[59] In addition, the low-temperature solution-processed CuCrO_2 nanocrystals as an HTL have a suitable electronic structure and charge-carrier transport properties. The PCE of 19.0% has been achieved through adopting the optimized CuCrO_2 as an HTL, which also exhibits a substantially enhanced photostability, thus avoiding the associated degradation.^[6] CuSCN was also reported by Grätzel et al.^[56] as an HTL for achieving highly efficient and stable PVSCs. The PVSCs with CuSCN HTLs show an efficiency over 20%, and can also retain 95% of the initial efficiency after 1000 h of continuous operation under conditions of full-illumination at 60 °C. The CuSCN -based PVSCs were reported to have efficiency comparable to the Spiro-OMeTAD-based PVSCs, and even better stability, using much cheaper materials and without the requirement of any additives for working as efficient HTLs. In addition, HTL-free and metal oxide-free perovskite solar cells with the HTL-free and metal oxide-free have also been reported and achieved comparable device performance and stability.^[54,100] The adoption of various HTL materials in perovskite solar

cells and their corresponding efficiencies are summarized in Table 2.

2.3. Low-Temperature Processing CTLs for Flexible PVSCs

The development of flexible PVSCs is required to extend the application of solar panels to indoor or wearable electronics. However, the flexible substrates normally cannot sustain the high-temperature processing such as 500 °C in preparation of compact TiO_2 in rigid PVSCs, so the low-temperature ETL and HTL are intensively investigated.

Regarding ETL, Kim et al.^[101] proposed the low-temperature processing of compact TiO_2 based on atomic deposition technique on a PET/ITO substrate at 80 °C, achieving PCE of 12.2%. Jeong et al.^[102] deposited the compact TiO_2 layer by UV-assisted solution process with a Nd-doped TiO_2 nanoink below 50 °C, resulting in a PCE of 16.01% for the best device. Zn_2SnO_4 has also been reported in high-performance flexible PVSCs due to its outstanding optical and electrical properties. The bilayer of Zn_2SnO_4 nanoparticles and Zn_2SnO_4 quantum dots yields an efficiency of 16.5%.^[26]

Low-temperature NiO_x -based HTLs are widely studied in flexible PVSCs. By spin-coating NiO_x nanocrystalline film on a PET/ITO substrate, the inverted PVSCs give an efficiency of 14.53%.^[103] Conventional organic HTL materials such as PEDOT:PSS are also reported in the flexible PVSCs. However,

Table 2. Summarization of the various hole transport layers for perovskite solar cells.

Hole transport material	Device structure	Physical	PCE	Ref.
PEOz-PEDOT:PSS	ITO/PEOz PEDOT:PSS/Perovskite/ PCBM/Bphen/Ag	Promoting perovskite with enlarged grain sizes, increasing the work function of the HTL, decreasing the noncapacitive current	17.39%	[14]
Ultrathin PEDOT	Ag/BCP/C ₆₀ /perovskite/ PEDOT/ITO	Transparency, conductivity, film morphology	19.3%	[12]
PEDOT:PSS-NH ₂ -OH	ITO/PEDOT:PSS-NH ₂ -OH/ CH ₃ NH ₃ PbI ₃ /PCBM/Al	Strong charge extraction capability, efficient hole transport, and excellent electron blocking	14.16%	[13]
DA-PEDOT:PSS	ITO/DA-PEDOT:PSS/perovskite/ PCBM/PN4N/Ag	Improve perovskite to HTL charge extraction capability and work function	18.5%	[11]
AMH-doped PEDOT:PSS	ITO/PEDOT:PSS (AMH)/ CH ₃ NH ₃ PbI ₃ perovskite/PC ₆₁ BM/Bphen/Ag	AMH dopant enhances the conductivity, changes the surface property	14.61%	[29]
OMe-TATPy	Au/OMe-TATPy/Perovskite/ cp-SnO ₂ /ITO	Improve charge delocalization and intermolecular stacking, but also potential trap passivation via Pb–S interaction	20.6%	[7]
Spiro-OMeTAD with TBA salts	FTO/TiO ₂ /meso-TiO ₂ /perovskite/ Spiro-OMeTAD with TBA salts or with LiTFSI and TBP/Au	The anions in the TBA salts improve the hole conductivity and uniformity	18.4%	[6]
BMPyTFSI	FTO/TiO ₂ /perovskite/Spiro-OMeTAD (BMPyTFSI)/Au	Increase the conductivity of Spiro-OMeTAD, reduces charge recombination	14.96%	[8]
Spiro-OMeTAD derivatives TET	FTO/SnO ₂ /C ₆₀ -SAM/ perovskite/TET/Au,	Facilitate efficient hole transport	19.0%	[9]
NiO _x	ITO/Zn-doped NiO _x / CH ₃ NH ₃ PbI ₃ / PC ₆₁ BM/bis-C ₆₀ /Ag	Zn has a similar atomic size with Ni and forms highly crystalline oxide materials	13.72%	[86]
np-NiO _x	Ag/PCBM/(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} / np-NiO _x /ITO	Favor the pinhole-free, highly textured, large grain size perovskite film	19.10%	[15]
Mesoporous NiO _x scaffold	glass/FTO/NiO _x /perovskite/ PC ₆₁ BM/BCP/Ag	Improve the contact between NiO _x and perovskite layers	16.7%	[9]
Cs/NiO _x	FTO/Cs/NiO _x /perovskite/ PCBM/BCP/Au	Cs enables holes to be efficiently separated at the interface and inhibition of recombination	17.2%	[85]
Co-doped NiO _x	ITO/Co-NiO _x /MAPbI ₃ / PCBM/Ag	Adjust the work function and enhance electrical conductivity of the NiO _x film	18.6%	[12]
LAD-doped PTAA	FTO/TiO ₂ /CH ₃ NH ₃ PbI ₃ / LAD doped PTAA/Au	Nonextrinsic Li ⁺ -ion migration and trap states at the perovskite surface passivated by LAD, high hydrophobicity, uniform HTL layer without	19.01%	[17]
CuPc	glass/ITO/TiO ₂ /passivation layer/ perovskite/CuPc/Au	Au-doped CuPc	20%	[98]
r-GO/CuSCN	Ag/BCP/PCBM/MAPbI ₃ / CuSCN/r-GO/ITO	Matched energy level, the r-GO/CuSCN bilayer prevent the recombination at MAPbI ₃ interface	14.28%	[16]
GO with Au and MoO _x NPs	Ag/BCP/PCBM/MAPbI ₃ / GO-Au NP/ITO	NPs increase the work function of GO	16.7%	[89]
MoS ₂	Al/PFN/PCBM/perovskite/ PTAA/MoS ₂ /ITO	MoS ₂ flakes between the PTAA HTM and the MAPbI ₃ toward ultrastable device	16.24%	[99]
CuCrO ₂	ITO/c-CuCrO ₂ /perovskite/ PCBM/BCP/Ag	Enhanced photostability, prevent the perovskite film from intense UV light exposure to avoid associated degradation	19.0%	[6]
V1050	FTO/SnO ₂ /FA _{0.83} CS _{0.17} Pb(I _{0.8} Br _{0.2}) ₃ / HTM/Au	Nonspiro fluorenebased hole transport materials V1050 and V1061	18.3%	[92]
S/FK209	Au/S/FK209/perovskite/ SnO ₂ /FTO	The iron complex is p-dopant, increase the Spiro-OMeTAD work function	19.5%	[10]

Table 2. Continued.

Hole transport material	Device structure	Physical	PCE	Ref.
G1 and G2	FTO/TiO ₂ /[HC(NH ₂) ₂] _{0.85} [CH ₃ NH ₃] _{0.15} Pb[I _{0.85} Br _{0.15}] ₃ /HTM/Au	Good film-forming properties, better interactions with perovskite, slightly deeper highest occupied molecular orbital, higher mobility, and conductivity	20.2%	[96]
Li-salt/4-tert-butylpyridine P3HT	Au/P3HT/perovskite/Meso-TiO ₂ /FTO	Improve the carrier density	17.55%	[95]
PVP	FTO/TiO ₂ /Cs0.05(MA _{0.17} FA _{0.83}) _{0.95} Pb(I _{0.83} Br _{0.17}) ₃ / PVP/Spiro-OMeTAD/Au	Reduce nonradiative recombination	20.9%	[97]
Disodium salt of substituted benzo	Ag/BCP/C ₆₀ /MAPbI ₃ /BDPSOs/ITO	Tunable orbital level and controllable solubility. Matched energy level with MAPbI ₃	17.2%	[95]

these devices normally show poor stability under ambient conditions.^[104]

3. Mobile Ions in PVSCs and Influence from CTLs

A large number of the mobile ions existing in perovskite materials will move in the perovskite layer in terms of drift and diffusion process and have the possibility of accumulating around the interface of the perovskite/CTL or penetrating into the CTL, and then accumulating around the interface of the CTL/electrode. In this part, we will discuss the potential influences of mobile ions on device performance and offer an in-depth understanding of manipulating these mobile ions.

3.1. The Influence of Mobile Ions on Device Performance: Hysteresis Phenomenon in PVSC

The anomalous hysteresis of *J*–*V* curves has been found earlier by Snaith et al.^[66] in PVSC devices. The current–voltage characteristics highly depend on the voltage scan protocol: rate, direction, and the precondition before starting the voltage scan. This phenomenon significantly influences the practical application of PVSCs, since the power output from the device will be hard to stabilize with a pronounced *J*–*V* hysteresis, thus casting doubt on the validity of the reported performance. Therefore, the origins of the hysteresis have become one of the crucial problems in this field of perovskite research. Regarding this, Snaith et al. proposed three possible origins:^[66] the very large defect density near or within the perovskite absorber surface, excess ions or ionic defects in the perovskite absorber, and the ferroelectric properties of the perovskite material. Based on intensive experimental and theoretical studies in the recent years, the ferroelectric properties of perovskite are unlikely to be crucial,^[105] while the charge trapping and de-trapping processes are able to explain some of the *J*–*V* hysteresis pattern,^[65] but without implementing the rate-dependent hysteresis with different scan very well. The timescale of hysteresis dynamics is more likely to match that of ionic dynamics. The mobile ion or ionic defects coupled with surface recombination are suggested to be an important factor contributing to the *J*–*V* hysteresis phenomenon thus affecting the device performance.

Earlier in this field, the concept of the hysteresis index was proposed to evaluate the degree of hysteresis of the

J–*V* curves of perovskite solar cells. However, depending on the device structure and the material properties, the hysteresis phenomena are too complicated to be described by a single index.^[106] Among the *J*–*V* hysteresis widely reported by different groups, the main features are summarized by Ravishankar et al. in ref. [64], as shown in **Figure 8**, and their descriptions are listed below:

- Capacitive hysteresis. The forward and backward scan *J*–*V* curves are systematically separated above and below the steady-state curve. Here, forward and backward scan refer to the voltage scan from 0 V or reverse bias to the voltage larger than *V*_{oc}, and the opposite direction. This phenomenon can be explained as the contribution of the capacitive current, which can also increase with the voltage scan rate.^[107–109]
- Current “bump” near *V*_{oc}. It has been widely observed that the current would be larger than the *J*_{sc} when the voltage is close to *V*_{oc}, during the backward scan. The current “bump” is direction and rate dependent and also highly correlated to the preconditioning bias.^[110]
- Larger *J*_{sc} for the backward scan. When increasing the scan rate in case (b), the photocurrent at 0 V will also be enhanced and be larger than *J*_{sc}.^[110]
- Strong decay of photocurrent in the case of forward scan. The strong photocurrent decay has been reported as a result of special polarization.^[111,112]
- Remarkable shunt resistance effect at low voltage. This depends on the bias, scan rate, direction, and temperature.^[63,113–115]
- Apparent *V*_{oc} shift. The forward scan curve shows a lower *V*_{oc} than the backward scan, in which the *J*_{sc} is not modified.^[116–118]
- Crossing between the forward and backward scan curves. In this case, the forward current may exceed the backward current in some region between 0 V and *V*_{oc}.^[108,116,117] unlike the other cases in which the discrepancy between the two scan-direction curves remains constant within the scan region.

These strong variations of the photocurrent and photovoltage in voltage scans highly depend on the quality of the perovskite layers and the interfaces. Based on the density function theory calculation, it is known that inside the typical MAPbI₃ the formation energies for iodine vacancies and methylammonium (MA) vacancies are sufficiently low to allow a high enough density of the two vacancies to exist at room temperature.^[119] It is also found then that the iodine vacancies are able to migrate in the perovskite layer through the device.^[120] Several physical understandings of the hysteresis phenomenon based on the concept of mobile ion (and contacts) were proposed.

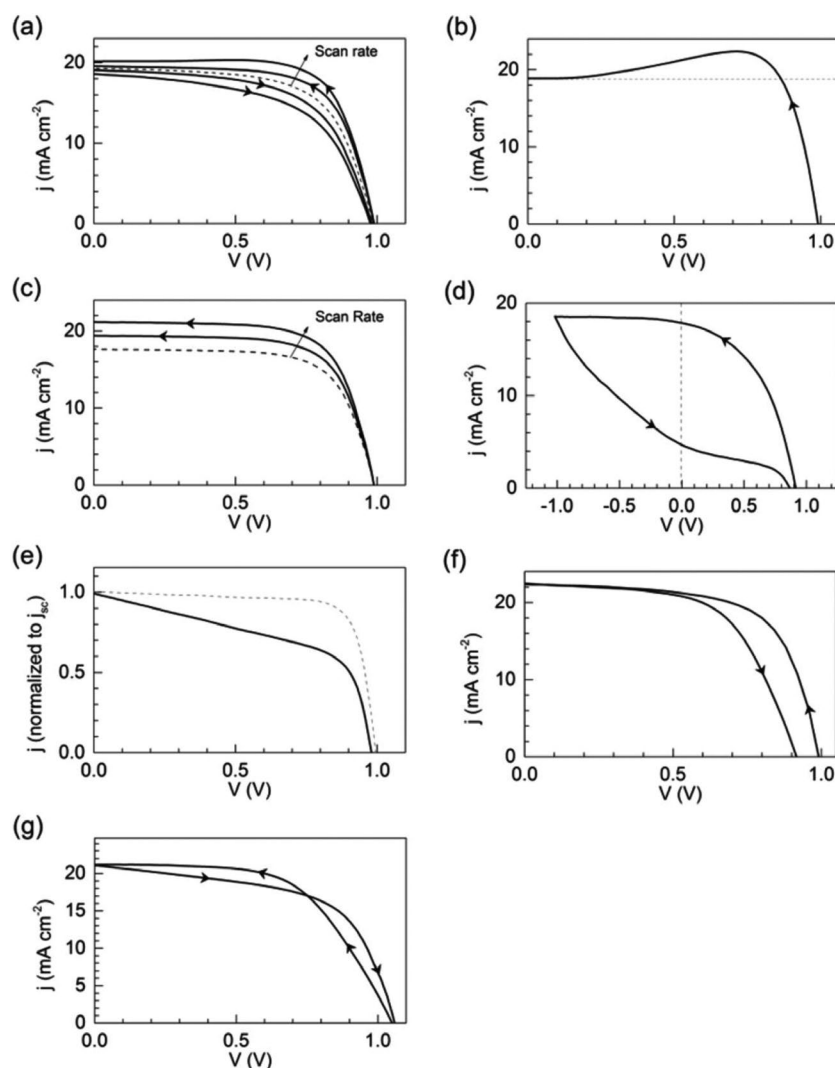


Figure 8. a–g) Summary of J – V hysteresis behaviors in perovskite solar cells. Arrows on the black solid lines indicate the forward and backward scan directions. Dashed lines in panels (a) and (c) refer to the steady-state curves, and in panels (b) and (d) show positions of short circuit current and zero-bias voltage, respectively. In panel (e), the dashed line shows the typical diode J – V curve. Reproduced with permission.^[64] Copyright 2017, American Chemical Society.

In the work of Tress et al.^[63] and Van Reenen et al.,^[65] the fundamental reason for hysteresis is attributed to the ion-induced electric field redistribution. In the p–i–n structured device, it is the built-in electrical field between the two electrodes that determines the carrier transport inside the device, which includes both the electronic carriers (electron and hole) and ionic carriers (positive ionic defect and negative ion). Due to the very large densities of positive ionic defects and negative ions ($\approx 10^{19} \text{ cm}^{-3}$,^[119] while the typical electron or hole density in bulk under bias voltage lower than V_{oc} is at least four orders of magnitude lower), the migration of ionic carriers along the built-in electric field will cause large charge accumulation near the interfaces, and therefore form space charge layers, which will then strongly screen the electric field. Screening of the electric field will induce a sharp drop in potential at the perovskite-contact interface, and then result in the nearly field-free region in bulk at the equilibrium state. Thus, the electric field will highly

depend on the applied voltage scan method which determines the drift of ion, and possibly prevents the electron and hole extraction at the respective electrodes, enlarges the recombination, and decreases the carrier collection efficiency, similar to the forward scan case in Figure 8b. Based on the scan method and the device structure, the electric field screening under the applied voltage is slowly modulated based on the ion migration and accumulation along with the built-in field.

This explanation is reasonable for the rate-dependent J – V hysteresis shown in ref. [63]. At very low scan rates, the change in the electric field change can compensate throughout the scan and result in a low hysteresis, while at an intermediate scan rate, the change in the electric field change is not sufficient enough, and results in a large hysteresis. For very fast scans, the slow mobile ion profile can hardly respond to the applied voltage change, and therefore the hysteresis decreases again. It should be noted that ion migration is necessary for the pronounced hysteresis but not sufficient, while the surface recombination at the perovskite-contact interfaces is also required.^[121] It should be noted that in the model proposed by Reenen et al.,^[65] the charge trapping and de-trapping processes are also important, but it was found that the timescale of charge trapping and de-trapping is much faster than the hysteresis dynamics, and without the consideration of charge trapping/de-trapping, people can still implement the J – V hysteresis.

Other than the discussion above, Ravishanker et al.^[64] proposed another explanation called the surface polarization model to further analyze some hysteresis phenomena related to contact layers, which are hard to explain simply by the screening of the electric field and ion redistribution. It is well-known

that the inverted PVSCs showed much lower hysteresis, and the perovskite-TiO₂ interface is reported to be more important than the perovskite-Spiro-OMeTAD interface in determining the hysteresis.^[122] These observed experimental results indicate the importance of the perovskite-contact interface properties. Rather than focusing on the energetic properties of the contacts (i.e., work functions and determining the built-in electric field), the surface polarization model emphasize the role of the surface capacitance of the perovskite-contact interfaces. In their model, it is the rate of arrival and departure of the ion at the interfaces that determines the hysteresis of the device. They distinguished in detail the surface polarization voltage from the external voltage, which is from band bending and is slowly changed by the internal kinetics at interfaces. Surface charge is determined by the surface polarization voltage, and then this additional charge will participate in the overall recombination process in the device. They modified the classical diode equation, which

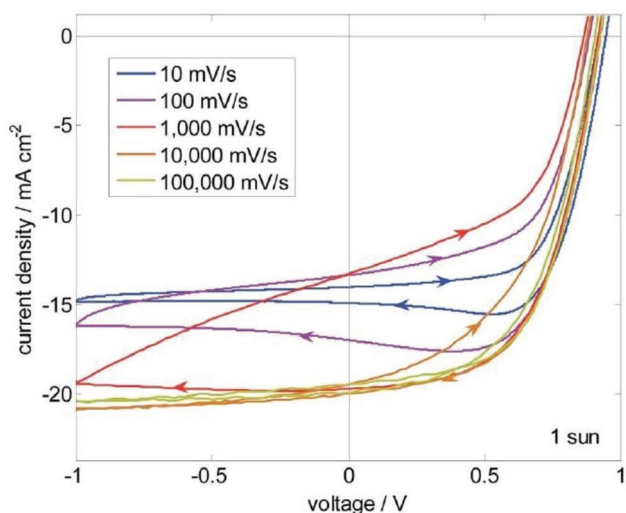


Figure 9. Current–voltage curves of TiO_2 -based $\text{CH}_3\text{NH}_3\text{PbI}_3$ devices with pronounced hysteresis. Arrows show the sweep direction. Voltage scans with different rates from 1 to -1 V and back to 1 V. Scan rates are from 10 to 100 000 $\text{m V}^{-1} \text{ s}^{-1}$. Reproduced with permission.^[63] 2015, Royal Society of Chemistry.

could be used to further fit the experimental J – V curves. In our opinion, this model is more reasonable for high-performance devices with good perovskite film quality, since in these cases, the energy loss during the carrier transport in bulk will be low enough and surface properties should dominate.

In addition to the different categories of hysteresis J – V curves summarized in ref. [64] and shown in **Figure 9**, the inverted hysteresis will be briefly reviewed below. Normally, the performance of a forward scan is reported to be better than that of a backward scan, but in some work,^[123–125] it is observed that the backward scan case performed better than the forward scan, with^[123] or without^[124] the S-shape in J – V curves. This “inverted” feature is not simply due to a different measurement protocol, but will still exist under various scan rate, preconditioning, and illumination, which indicates that this feature has fundamental origins in the material properties and device structure. Tress et al.^[123] attributed the observed inverted hysteresis to the energy extraction barrier at the perovskite/ TiO_2 interface under 0 V in their devices, which will benefit the carrier collection and increase the performance of the forward scan. The “inverted” feature can also be explained by the two physical models mentioned above: in some devices, the existence of the additional energy barrier or another surface property such as surface recombination due to surface charge, will influence or even invert the effect of ion migration on the carrier transport and thus deliver two different perovskite-contact interfaces, therefore causing the different hysteresis features. The change in hysteresis by the modification of the TiO_2 layer can also support this statement.^[126]

3.2. Design of CTLs for Reducing Hysteresis

Although the exact reason for the hysteresis effect is still not completely clear, it is widely accepted that the ion migration is

strongly correlated to the origin of hysteresis. Therefore, the most straightforward method to suppress hysteresis is to control the effect of ion motion, i.e., diminishing the ion migration itself or decreasing its effect by interfacial engineering.

Among the methods reported focusing on this problem, interfacial engineering based on the incorporation of fullerene (e.g., PCBM) is one of the most successful. Either by inserting PCBM as an interlayer, or mixing PCBM in the solvents to form the bulk-heterojunction like the structure of perovskite, a hysteresis-free device can be obtained.^[38,127,128] The optimizations through the incorporation of PCBM are usually attributed to trap passivation in the bulk or at the perovskite-contact interfaces, or reaction with the iodide anions, or just filling the defects which would be the ion migration channels.^[129] It should be noted that another possible reason for reducing hysteresis by PCBM is the electrical optimization of the interfaces. On the one hand, the perovskite/PCBM interface shows better carrier extraction efficiency than the perovskite/ TiO_2 interface, as proved by the transient PL study.^[130] Both models reviewed in the former section indicate that more efficient of carrier extraction at the interfaces can help to reduce the effect of ion migration. On the other hand, the lower permittivity of PCBM (10 times lower than TiO_2) ETL will lead to a lower potential drop in the perovskite layer,^[131] which will also change the built-in electric field distribution and reduce hysteresis.

As we mentioned in the above section, for the classical device structure with TiO_2 as the ETL, the perovskite/ TiO_2 interfaces are more important in determining the hysteresis of the device than other interfaces such as perovskite/Spiro-OMeTAD, and one possible reason is the larger surface capacitance of the perovskite/ TiO_2 interface.^[64] Therefore, the modification of TiO_2 layer will also be beneficial for approaching hysteresis-free device. Earlier in 2015, J.H. Heo et al.^[130] reported a Li-treated mesoscopic TiO_2 ETL could help to achieve the hysteresis-free PVSCs, through the better carrier transport and lower trap density in Li-treated mesoscopic TiO_2 . The energy alignment of the perovskite- TiO_2 interface is also adjusted for more efficient carrier extraction. Similarly, Zr-incorporated planar TiO_2 ETL is also reported to reduce hysteresis compared with the device with bare TiO_2 layer, by reducing the surface recombination. Large carrier lifetime has been observed in the transient photocurrent measurement.^[132] The Cl-capped TiO_2 colloidal nanocrystal film working as planar ETL can significantly reduce the hysteresis,^[133] by approaching efficient surface passivation of the trap at perovskite/ TiO_2 interface and then lowering surface recombination. The cobalt-doped TiO_2 ETL is also reported to produce hysteresis-free PVSCs, by passivating the surface trap or sub-band-gap states.^[134]

To combine the advantages of the efficient carrier extraction of fullerene-based ETL and the high conduction of TiO_2 ETL, the fullerene-incorporated TiO_2 ETL has been reported extensively in recent years.^[135] Modifying the planar TiO_2 layer by self-assembled monolayer C_{60} ^[136] can significantly passivate the nonradiative recombination centers at the perovskite- TiO_2 interface. Therefore, dramatically increasing electroluminescence was observed in the device incorporated with C_{60} . Planar PCBM/ TiO_2 ETL is also reported^[137] to reduce the hysteresis for a similar reason. Very recently, H. Jiang et al.^[38] reported that simultaneously doping of the perovskite and modifying

the perovskite/TiO₂ interface by PCBM, which can reduce the bulk recombination and surface recombination, then efficiently improve the device performance and reduce the hysteresis. Y. Zhao et al.^[81] reported the PVSCs with fullerene-decorated TiO₂ layer as planar ETL, which can achieve the high efficiency, long-term stability, and less hysteresis. The fullerene decorating the TiO₂ helps to passivate the trap and fill the void, thus achieving the lower surface recombination as well as efficient ion-blocking.

Meanwhile, it was also demonstrated that CTLs are particularly important for the stability of PVSCs. Apart from the reversible degradation according to hysteresis, the irreversible degradation of PVSCs is mainly attributed to the chemical properties of materials, particularly those of the CTLs since the characterization of the interfaces between perovskite and CTLs can be highly influenced by many factors. As reviewed in Section 2, different types of materials for ETL and HTL, with different treatments, will cause very different stabilities of the devices. It is also well-known that even the similar methods in different laboratories result in different stabilities, as it also depends on the purity of material and the fabrication conditions. Therefore, the effects of CTLs should be well understood to avoid both the reversible and irreversible degradations.

4. Theoretical Understanding of PVSC by Device Modeling

4.1. Prediction of the Efficiency Limit and Quantification of Efficiency Loss

Although considerable progress has been made in recent years to boost the PCE of PVSC to 23.7%,^[1] a fundamental

analysis is still required to better understand the factors that limit the performance of PVSCs to approach the radiative efficiency limit.^[138] Sha et al. have shown that the efficiency limit of MAPbI₃ based PVSCs is 31%,^[139] with the help of their detailed balance model, in which the light-trapping effect and the angular-restriction design have also been discussed. Ren et al.^[140] have also predicted the same efficiency limit by the modified drift-diffusion model. Pazos-Outon et al.^[141] continued to develop the detailed balance model for MAPbI₃ devices by further considering both Auger recombination, which plays an important role in the silicon solar cells, and SRH recombination, for the more practical predication. They found that the competitions between the radiative recombination and Auger recombination determine the maximum achievable external luminescence efficiency, and therefore the performance limit of the material. Auger recombination in MAPbI₃ devices can reduce the external luminescence efficiency to ≈95% of the limit, and result in the Auger efficiency limit of 30.5%, which indicates that Auger recombination has very little effect on the efficiency limit of MAPbI₃ devices. The crucial factor that limits the efficiency is still the non-radiative recombination (Shockley-Read-Hall (SRH) recombination), as shown in **Figure 10**. Only beyond the recombination lifetime of 100 μs can the PVSCs approach the efficiency limit.

Baloch et al. proposed a more practical efficiency limit in ref. [142] by considering the extreme reported values of the radiative recombination rate (B) and nonradiative recombination (SRH recombination) rate (U_{SRH}) using the software SCAPS. Four cases are considered in their analyses, and in each case the minimum or maximum recombination rates B and U_{SRH} are preset as a combination in the model, as shown in **Figure 11**. With the more realistic simulation parameters,

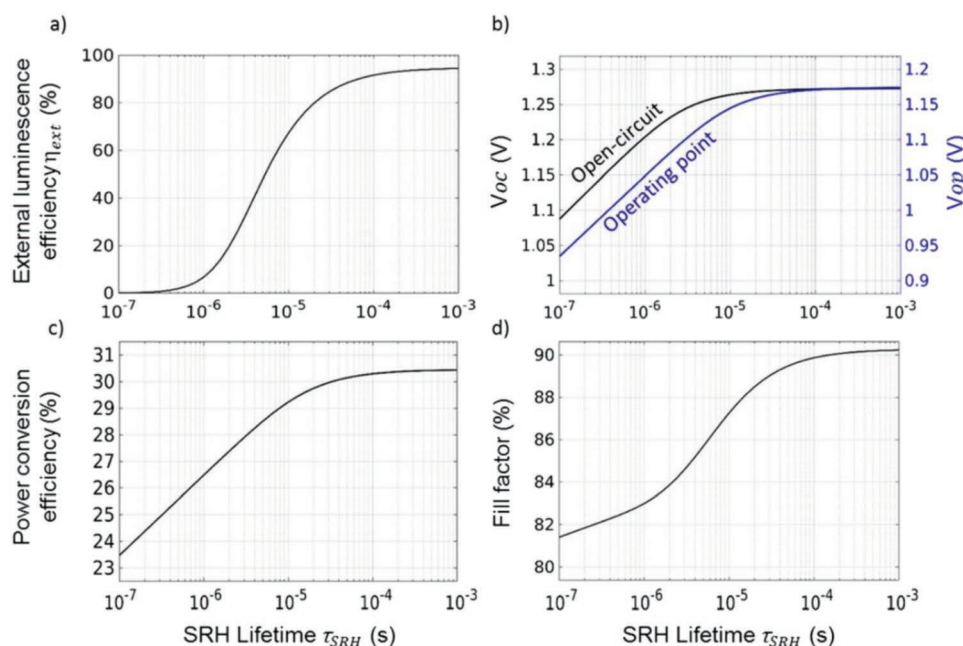


Figure 10. Performance limit of the a) external luminescence efficiency, b) open-circuit and operating point voltages, c) power conversion efficiency, and d) fill factor versus SRH lifetime. This is calculated for a textured 500 nm thick device with a perfect rear mirror under 1 sun illumination. Reproduced with permission.^[138] Copyright 2018, American Chemical Society.

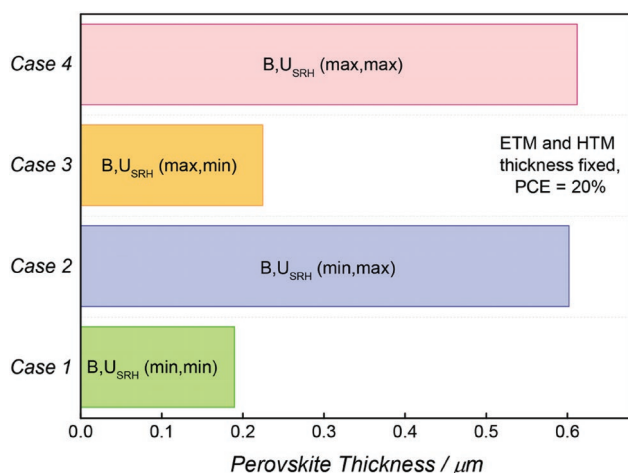


Figure 11. Optimum perovskite absorber thickness to achieve a PCE of 20%. Fixed thicknesses of TiO_2 and Spiro-OMeTAD at optimum values were considered. The required perovskite thickness was 0.19 μm for Case 1, 0.60 μm for Case 2, 0.22 μm for Case 3, and 0.61 μm for Case 4. Reproduced with permission.^[142] Copyright 2018, American Chemical Society.

they reported the optimum thicknesses of the PVSC absorbers in each case. A higher recombination will induce more energy losses in the bulk, and a thicker absorber layer therefore is required to maintain the high efficiency.

Based on the modeling techniques and the physical understanding of the factors that limit the PCE, further analysis of efficiency loss has been reported. Sha et al. modified the detailed balance model to quantify the efficiency loss of the optimized and highly efficient perovskite solar cells.^[62] The modified detailed balance model is expressed as

$$J = \frac{V - J R_s}{R_{\text{sh}}} + J_n(V - J R_s) + J_r(V - J R_s) - J_p \quad (1)$$

where R_s and R_{sh} refer to the series and shunt resistances, J_n and J_r are the current loss due to the radiative emission and nonradiative recombination, and J_p is denoted as the photocurrent, which

can be obtained by numerically solving Maxwell's equation. The photo-recycling effect is also included. For a given J - V curve, one can adopt the model to fit the nonradiative recombination factor, series, and shunt resistances to analyze the efficiency loss. In the analysis of real devices, the so-called efficiency loss is quantified with reference to the performance of the ideal device achieved at the radiative efficiency limit. As shown in Figure 12a, the efficiency loss of PVSC highly depends on the recombination loss and R_s , R_{sh} loss, while the optical loss remains almost unchanged. To analyze the effects of CTLs in PVSCs, NiO_x , PEDOT:PSS (as the HTL) and C_{60} , Bis- C_{60} and ZrAcAc (as the ETL) are applied in the experiments, and efficiency losses of different ETL/HTL combinations are calculated by the model. Based on the changing series and shunt resistance and optical reflectance, different CTLs can influence the efficiency loss from several aspects. For the optimized PVSCs with PCE > 19%, the efficiency loss analysis is shown in Figure 12b. The optical loss can be suppressed to only 25%, and the dominant factors become the losses from the resistances and nonradiative recombination, which indicates the importance of the CTLs.

In addition, some new circuit models have also been proposed for the study of PVSCs. Liao et al.^[67] reported a double PN junction circuit model to consider the band bending at the two perovskite interfaces, as shown in Figure 13. This new model can focus more on the ideality factor and the carrier recombination from the interface defects and will be more appropriate for fitting the dark current.

4.2. Insight of the Mobile Ions on Device Performance

The drift-diffusion model is widely used for the study of carrier dynamics in solar cell research from the traditional silicon solar cells to the emerging PVSCs. The classical drift-diffusion model consists of the continuity equations for the electron and hole, and Poisson's equation describing the potential distribution. These equations can be solved numerically to obtain the charged carrier distribution, and the energy band diagram inside the device, as well as the output current in response

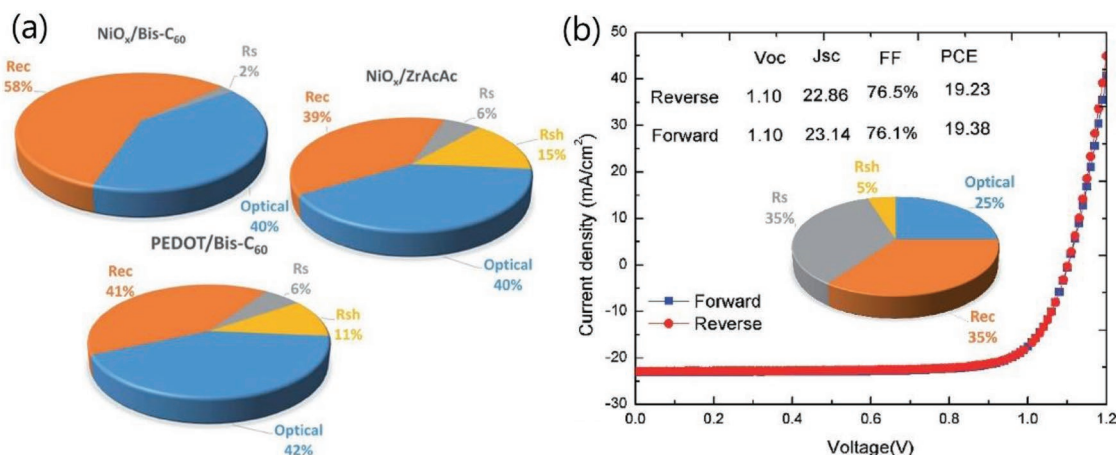


Figure 12. a) The dependence of the efficiency loss of PVSCs on carrier transport layer configuration. b) Efficiency loss of high-performance PVSCs with the device structure: ITO/ NiO_x (20 nm)/ $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ (300 nm)/PCBM: C_{60} mixture (50 nm)/Bis- C_{60} (10 nm)/Ag (120 nm). Reproduced with permission.^[62] Copyright 2018, Wiley-VCH.

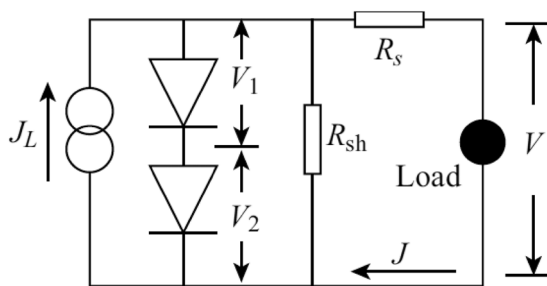


Figure 13. Schematic of the new double PN junction model. Reproduced with permission.^[67] Copyright 2018, Springer.

to the bias voltage. However, a special configuration needs to be incorporated into the classical drift-diffusion model due to the pronounced influence from the mobile ionic defect. Van Reenen et al.,^[65] Richardson et al.,^[111] Jacob et al.,^[143] and Calado et al.^[121] have incorporated the continuity equation of the mobile ionic defect in the drift-diffusion model to study the ionic charge transport problem and the related transient responses of the perovskite solar cells such as J - V hysteresis. The mobile ionic defects incorporated model is formulated as

$$\frac{\partial n}{\partial t} = \frac{1}{q} \frac{\partial J_n}{\partial x} + G_n - U_n; J_n = -q\mu_e \left(n \frac{dV}{dx} - k_B T \frac{dn}{dx} \right) \quad (2)$$

$$\frac{\partial p}{\partial t} = -\frac{1}{q} \frac{\partial J_p}{\partial x} + G_p - U_p; J_p = q\mu_p \left(p \frac{dV}{dx} + k_B T \frac{dp}{dx} \right) \quad (3)$$

$$\frac{\partial a}{\partial t} = \frac{1}{q} \frac{\partial J_a}{\partial x}; J_a = q\mu_a \left(a \frac{dV}{dx} + k_B T \frac{da}{dx} \right) \quad (4)$$

$$\frac{\partial^2 V}{\partial x^2} = -\frac{q}{\epsilon_0 \epsilon_r} (n - p - a + N_{\text{static}} + N_A - N_D) \quad (5)$$

where Equations (2)–(4) are the continuity equations and current equations for the electron (n), hole (p), and positive ionic defects (a), and Equation (5) is the Poisson's equation considering both the mobile and static ionic charge. It should be noted that in most of the numerical studies, both mobile and static ionic charges are confined in the perovskite layer, which means that the carrier transporting layers have a completely ion-blocking property, and the perovskite interfaces are impermeable to the ionic charge. Einstein's relation is applied for electron, hole, and ionic defect, and there is no source and drain for the ionic defect. Equations (2)–(5) can be coupled and solved by the MATLAB pdepe toolbox,^[121] and self-built solver,^[65,111,112] or by software such as SCAPS.^[144] Neukom et al.^[145] proposed the ion incorporated drift-diffusion model by solving the ion continuity equation first to simulate the preconditioning treatment in the experimental measurement, and then solving the electron and hole continuity equations to model the current-voltage characteristics. This method avoids the numerical difficulty of solving the fully coupled drift-diffusion model and is able to work for the fast scan J - V simulation, due to the assumption that the ion would not move significantly during the voltage

scan. Some other theoretical studies of carrier dynamics based on the drift-diffusion model without ionic charge have also been reported.^[146,147] Differently, they did not focus on the ion migration but its effects on the traps, grain boundaries, and recombination.^[146]

4.3. Modeling Study of CTLs in PVSCs

As mentioned in the previous sections, the effects of CTLs in PVSCs are intensively studied in experiments. Here, we will also review the recent modeling works focusing on the physical properties of CTLs in PVSCs.

Earlier in 2015, Takashi Minemoto et al.^[148] studied the effects of energy level alignments of CTLs on the carrier transport and then the device performance by a 1D drift-diffusion simulator. Their study mainly focused on the band offsets between ETL/perovskite and perovskite/HTL, which should be important in determining the surface recombination together with the trap density at the interface of perovskite. Negative (forming the cascade energy band) and positive (forming an energy spike) band offsets of different values were carefully simulated, and the optimum positions of the conduction band and valence band of ETL and HTL were derived to be 0.0–0.3 eV higher and 0.0–0.2 eV lower than the corresponding bands of perovskite, respectively. Xiaoqing Wei et al.^[149] also put forward the full-device simulation of PVSCs including the effects of CTLs, but their study still focused on the band offsets.

Bisquert et al.^[150] proposed further understandings of CTLs in PVSCs with theoretical studies. Based on their ion-incorporated drift-diffusion simulation of the p-i-n heterojunction structure, the influence of CTLs on carrier accumulation under OC and SC conditions were discussed. Under steady OC condition, a strong accumulation of electrons and holes at each side of the perovskite/ETL interface is formed naturally, and the degree of accumulation depends on the discontinuity of the conduction band, the intensity of surface and bulk recombination and the free carrier mobility. The carrier distribution near the perovskite/HTL interface is the same. In the SC condition, the presence of ion accumulation near the interfaces has a pronounced field-screening effect and thus causes the carrier accumulation mainly at the perovskite/HTL interface. In particular, their study connects the properties of CTLs, such as carrier mobility, energy band, and recombination, to the experimentally observed high-values of low-frequency capacitances.

In addition to the full-device modeling study, the simulation of the experimental characterization of the perovskite/CTL interface such as the transient photoluminescence (tr-PL), is also helpful in understanding the device physics of CTLs. Thomas Kirchartz et al.^[151] proposed a transient drift-diffusion simulation for the MAPbI₃/PC₆₁BM heterojunction as a function of laser influence and interface properties. By comparing the simulation with experimental results, it was confirmed in their study that the nonlinear property of tr-PL contains two parts: the fast carrier transfer part, followed by the relatively slow carrier recombination part. The first part is determined by the carrier extraction property of CTL, while the second depends on the interface and bulk recombination. They also indicated that the surface recombination velocity of the MAPbI₃/PC₆₁BM

heterojunction should be $\approx 200 \text{ cm s}^{-1}$ to match well with the experimental data.

4.4. Outlook of the Device Modeling in Understanding the PVSC Device Physics

So far, the study of device physics of PVSCs by device modeling mainly focuses on the carrier dynamics inside the perovskite layer and at the perovskite/contact interfaces, including the ion migration and the related surface recombination and capacitance mechanisms. However, it has already been reported that the ionic charges are not confined in the perovskite layer, on the contrary, the diffusion of ions in the charge transport layers under different bias conditions is observed,^[152,153] which should be one possible reason for the reversible device performance degradation. Therefore, the careful consideration of the ionic charges diffusion inside the charge transporting layers in the device modeling is desired for better capturing the effect of ion migration on the PVSC performance, and the corresponding characterization methods are also required to unveil the fundamental reason of the long-term and reversible device performance degradation.

5. Conclusion

This work provides a review of the device physics of CTLs in PVSCs. The influence of the carrier transport material in determining the interfacial properties at the anode/HTL, HTL/perovskite and cathode/ETL, ETL/perovskite on device performance, and the strategies for improving the interface qualities are summarized. The influences of mobile ions on device performance and stability are also discussed. In addition, we reviewed the recent theoretical works on unveiling the device physics of PVSCs and the related CTLs, which will offer design rules with the potential to stimulate a much broader interest for high-performance PVSCs and other perovskite-based optoelectronics.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

device physics, interfacial engineering, perovskite solar cells

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