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Progress of interface engineering in perovskite solar cells

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ABSTRACT Organic-inorganic hybrid halide perovskite materials have been a suitable active layer in solar cells due to the extraordinary photonic and electronic properties. Perovskite solar cells (PSCs), no matter conventional structure or inverted structure, contain several key interfaces, including electrode/electron transport materials (ETM) interface, ETM/perovskite interface, perovskite/hole transport materials (HTM) interface, HTM/electrode interface. The interface is vital to the overall performance of the devices, since the exciton formation, dissociation, and recombination are directly related to the interface. Moreover, the degradation of devices is also highly sensitive to the interface. As a result, the deep understanding of the interfacial charge transfer and corresponding interfacial engineering is extremely important to achieve high-performance and high-stability PSCs. This review mainly focuses on the recent progress of interfacial engineering in PSCs, including conventional structured PSCs, PSCs employing carbon counter electrode, and inverted structured PSCs.

Keywords: perovskite solar cells, interface engineering, stability, charge transfer

INTRODUCTION

The energy crisis is one of the most urgent issues to be solved. Solar energy, as clean and sustainable energy source, could provide 10,000 times of power for the entire planet, highly suitable to replace the non-renewable fossil energy. With the aid of the discovery of photo-electrical effect, photovoltaic (PV) technology is an effective method to make use of solar energy, which could directly convert sunlight into electricity. So far, solar cells based on silicon (Si), gallium arsenide (GaAs), cadmium telluride (CdTe), and copper indium gallium selenide (CIGS), have achieved power conversion efficiencies (PCEs) over 20% [1]. Due to the high cost of the current photovoltaic technology, novel materials and device structure to further advance

photovoltaic technology are still necessary.

Organic-inorganic perovskite materials were first explored by Mitzi *et al.* in 1990s [2,3]. Their pioneering work sets up a solid foundation for these kinds of materials and device design. Perovskite solar cells (PSCs), were firstly reported by Kojima *et al.* [4], who employed $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ (MAPbBr_3) as sensitizers in liquid-electrolyte based dye-sensitized solar cells and achieved an efficiency of 3.81%. After that, the community in PV field paid a lot of attention to the organic-inorganic hybrid halide perovskite materials due to the extraordinary photonic and electronic properties [5–8]. By less than 10 years development, the efficiency has been raised to 22.1% according to the latest chart of record cell efficiencies from the National Renewable Energy Laboratory [1]. The efficiency rivals the emerging thin film technologies, such as CdTe (22.1%) and CIGS (22.3% without concentrator, 23.3% with concentrator). The amazing performance for organic-inorganic hybrid halide perovskite is attributed to the excellent properties, including its direct band gaps, high absorption coefficient, long carrier diffusion length, and ambipolar carrier transport property [9–11].

To push the rising star from academic studies into real life applications, the efficiency and lifetime are two major factors to be concerned. Wei and co-workers [12] predicted the efficiency limit of PSCs, considering the light trapping and angular restriction. For a 500 nm thick perovskite film with flat and perfect mirror surface, which is also the case for a standard PSCs, the open-circuit voltage (V_{oc}) is predicted to be 1.315 V, the short-circuit current (J_{sc}) to be 25.27 mA cm^{-2} , fill factors (FF) to be 0.91, and thus the final PCE to be 30.06%. The current performance is far from the ceiling. Moreover, many scientists and industrialists criticize the stability of PSCs, since

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many studies reported the sensitivity of perovskite to moisture, oxygen, light soaking, heat, and electric field [13–17]. Thereby, massive efforts have been paid to the improvement of performance and stability, such as film fabrication method, composition control, encapsulation, and interfacial engineering. For example, one-step and two-step solution processed method [8,18], vacuum deposition method [19], vapor-assisted solution processed method [20], and solvent engineering [21,22] have been developed to achieve perovskite films with flat surface, full coverage, and good crystallinity. In terms of composition control, for a typical perovskite materials with chemical formula ABX_3 , A can be replaced by Cs^+ , and $HC(NH_2)^{2+}$ (FA), B can be Pb^{2+} , Sn^{2+} , Ge^{2+} , and X can be Cl^- , Br^- , and I^- [9]. Both film fabrication and compositional control have contributed a lot to the development of PSCs. However, the interfacial design still lacks systematical study, which is beneficial to the understanding of working mechanism, as well as the device performance.

PSCs, no matter conventional structure or inverted structure, contain several key interfaces, including electrode/electron transport materials (ETM) interface, ETM/perovskite interface, perovskite/hole transport materials (HTM) interface, HTM/electrode interface. The interface is vital to the overall performance of the devices, since the exciton formation, dissociation, and recombination are directly related to the interface. Moreover, the degradation of devices is also highly sensitive to the interface. For example, Guerrero and co-workers [23] showed the degradation of the metal contact due to the ionic movement in the perovskite layer. As a result, the deep understanding of the interfacial charge transfer and corresponding interfacial engineering is extremely important to achieve high-performance and high-stability PSCs. This review mainly focuses on the recent progress of interfacial engineering in PSCs, including conventional structured PSCs, PSCs employing carbon counter electrode, and inverted structured PSCs. For conventional structured PSCs and PSCs with carbon counter electrode, the devices used n-i-p structure, which means ETM would receive the illumination, while the inverted structured PSCs used p-i-n structure with HTM receiving illumination, as shown in Fig. 1b. Fig. 1a summarizes the energy level of perovskite materials and commonly used interlayers.

CONVENTIONAL STRUCTURED PSCs

Interface engineering at the ETM/perovskite interface

Currently, there are three key issues for ETM/perovskite in-

terface in conventional structured PSCs: energy level alignment, perovskite films morphology control, and device stability. The interface engineering at this interface is conducted before perovskite film formation.

The interface between the absorber and ETM is important for the efficient carrier transportation. Proper energy level alignment at the perovskite/electrode interface has been credited for achieving simultaneously enhanced charge collection efficiency and V_{oc} of devices. The interface modification is an efficient route to tune the energy level alignment. The conduction band minimum (CBM) for a broad range of perovskites is in relatively matching energy alignment with the CBM of TiO_2 . Some additional interface engineering could be implemented in order to minimize losses in V_{oc} at this junction [24]. Zhou and co-workers [7] improved the electron transport channel in the device by using yttrium-doped TiO_2 as ETM to enhance its carrier concentration. It should be noted that, a thin polyethylenimine ethoxylated (PEIE) layer was inserted between indium tin oxides (ITO) and ETM to tune the ITO work function for facilitating charge extraction, resulting in a final PCE of 19.3%. Wang and co-workers [25] employed nanocomposites of graphene and TiO_2 nanoparticles as ETM, resulting in improved FF and PCE. They attributed the performance enhancement to the increase of conductivity of ETM or to a reduction in contact resistance, either at the ETM/perovskite, or FTO/ETM interface (Figs 2a and b).

Besides energy level and conductivity, the deep trap states on TiO_2 surface could cause some detrimental issues, such as charge recombination and poor stability. Nagaoka and co-workers [26] observed longer carrier lifetimes and higher charge carrier densities in devices based on Zr- TiO_2 electrodes, resulting in improved device performance. Wojciechowski and co-workers [27] reported that the electron transfer from perovskite to TiO_2 in standard planar PSCs was very slow. By modifying the surface of the TiO_2 compact layer with C_{60} self-assembled monolayer (C_{60} -SAM) molecules, the electron transfer was enhanced and both the n-type and p-type heterojunctions with the perovskite were active in driving the photovoltaic operation. In addition, C_{60} -SAM could passivate the formation of trap states on the perovskite side by the fullerene moiety, reducing the non-radiative recombination channels at this interface. Similarly, Lee's group [28] deposited [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM) onto the ZnO electrode, and the V_{oc} values of the devices with ZnO/PCBM substrates increased to ~ 1.03 V (compared to the devices with only ZnO 0.83 V). The enhancement was

Figure 1 (a) Scheme of the energy level for perovskite materials, electron transport materials, and hole transport materials. (b) Several typical structures of perovskite solar cells.

due to the modified electronic structure of the ZnO layer, as evidenced by the results of photoelectron spectroscopy analysis. In addition, trap-assisted charge recombination at the interface of ZnO and in the bulk of perovskite absorber was also effectively suppressed. Zhang and co-workers [29] proved that the oxygen vacancies in TiO₂ electrode could slow down charge extraction, while speed up the charge recombination at ETM/perovskite interface. By annealing TiO₂ at 1 atm oxygen partial pressure or pretreating TiO₂ by O₂ plasma, the original oxygen vacancy sites could be effectively filled and the hysteresis could be suppressed. Li and co-workers [30] synthesized a triblock fullerene derivative (PCBB-2CN-2C8) to modify TiO₂ surface, significantly improving charge extraction from the perovskite layer (Figs 2c and d).

The perovskite film morphology, such as coverage, crystallinity and preferred orientation, which is affected by ETM/perovskite interface, is highly related to the device performance. In order to enhance the coverage of perovskite on the ZnO nanorods, Zuo and co-workers [31] deposited 3-aminopropanoic acid SAMs on the ZnO surface to improve morphology of the perovskite film and

increase the light absorption, contributing to a 31% surge in the PCE value (Figs 3a and b). Ke and co-workers [32] reported the realization of efficient PSCs grown directly on fluorine-doped tin oxide (FTO)-coated substrates without using any hole-blocking layers. With the aid of ultraviolet-ozone treatment for FTO, the perovskite film exhibited large grains, a low density of pin holes, as well as a smooth surface. Li and co-workers [33] demonstrated a novel intermixing-seeded growth technique to obtain high-performance planar heterojunction PSCs (Figs 3c–f). Through interfacial engineering with ligand-exchange treatment, a small amount of methylammonium iodide (MAI)-capped PbS nanoparticles intermixed with the perovskite precursor solution, serving as nucleation sites to promote the formation of the inorganic framework of perovskite lattice structures. Finally, the morphology and PCE of the planar heterojunction PSCs were substantially improved.

During the process of assembling and testing, oxygen and moisture in the atmosphere can directly affect the stability of the components. Firstly, due to the hygroscopicity of CH₃NH₃PbI₃, it tends to hydrolyze in the presence of

Figure 2 (a) Series resistance, R_{series} , and (b) recombination resistance, R_{rec} , obtained from impedance spectroscopy analysis of samples with two different concentrations of graphene mixed with TiO_2 in the electron collection layer. Reprinted with permission from Ref. [25], Copyright 2014, American Chemical Society. (c) The steady-state PL spectra of perovskite film on TiO_2 and TiO_2 /PCBB-2CN-2C8. (d) TRPL decay transient spectra of ITO/ TiO_2 /perovskite and ITO/ TiO_2 /PCBB-2CN-2C8/perovskite. Reprinted with permission from Ref. [30], Copyright 2015, American Chemical Society.

Figure 3 Influence of interface modification at ETM/perovskite interface on morphology control. SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskites on (a) bare ZnO and (b) ZnO/C3-SAM. Reprinted with permission from Ref. [31], Copyright 2015, American Chemical Society. (c-f) SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ thin films without and with the inclusion of the indicated concentrations of PbS nanoparticles. Reprinted with permission from Ref. [33], Copyright 2016, the Royal Society of Chemistry.

moisture, forming $\text{CH}_3\text{NH}_3\text{I}$, CH_3NH_2 , HI, and PbI_2 in the film. There are two routes for HI to degrade in the next step. One is a redox reaction in the presence of oxygen; the other is a photochemical reaction, in which HI can decompose into H_2 and I_2 under UV radiation. The consumption of HI, drives the whole degradation process forward [14]. Secondly, the surface adsorption of H_2O or hydroxyl onto TiO_2 is an alternative way. Our group introduced the magnesium oxide (MgO) layer onto TiO_2 , reducing the amount of H_2O [34]. In addition, MgO at the interface blocked direct contact between TiO_2 and perovskite, thus suppressing the perovskite degradation under H_2O and UV conditions. Previous study identified that the instability in mesoporous TiO_2 -sensitized solar cells arose from light-induced desorption of surface-adsorbed oxygen [35]. The efficiency decrease in the TiO_2 /perovskite structural solar cells is especially prevalent when the cells are encapsulated in an inert atmosphere. Li and co-workers [36] used caesium bromide at the interface between TiO_2 and perovskite, effectively enhancing the stability of planar heterojunction devices under UV light soaking (Fig. 4). Moreover, Sb_2S_3 was also used as the insulating layer to protect perovskite [37]. During the light exposure test without encapsulation, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells without Sb_2S_3 deteriorated to zero efficiency in 12 h and were completely changed from black to yellow. With Sb_2S_3 deposited, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells became stable against light exposure without encapsulation.

Interface engineering at the perovskite/HTM interface

As documented in last section, the ETM/perovskite interface is related to the electron extraction process, perovskite morphology control, and device stability. As an i-p junction, the perovskite/HTM interface has similar impacts on device performance, such as stability and hole extraction process.

For conventional structured PSCs, 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenyl-amine)9,9'-spirobifluorene (spiro-MeOTAD) is the most widely used HTM. However, due to the limited conductivity of pure spiro-MeOTAD, oxygen exposure is necessary for high performance devices. In order to expedite the oxidative reaction between spiro-MeOTAD and O_2 , lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) is needed as a counterion [38]. 4-Tert-butylpyridine (TBP) is another additive added into spiro-MeOTAD to improve the open-circuit voltage. However, TBP and acetonitrile which are the solvent to dissolve LiTFSI , could degrade perovskite. Much attention has been paid to improve the stability of perovskite toward

Figure 4 The UV stability of the TiO_2 /perovskite thin films modified with and without CsBr. Reprinted with permission from Ref. [36], Copyright 2016, the Royal Society of Chemistry.

spiro-MeOTAD and prevent charge recombination by interfacial modification in this interface.

Our group systematically studied the corrosion of perovskite by TBP. Upon the dropping of TBP, the film rapidly faded and decomposed by the dissolution of PbI_2 in TBP (Fig. 5a). We used montmorillonite (MMT) with an intercalated structure as a buffer layer to protect perovskite from corrosion by TBP [39]. Infrared spectroscopy (IR) and X-ray diffraction (XRD) results demonstrated that MMT could interact with TBP through hydrogen bonds in its intercalated structure. UV-vis spectra showed the preserved perovskite absorption after TBP treatment for MMT modified sample (Figs 5b and c). Considering the corrosion effect of TBP, we tried to decrease its concentration in spiro-MeOTAD solution. Unfortunately, the solution was hard to spread out on the perovskite surface. Our group introduced graphene oxide (GO) at the interface between perovskite and HTM [40]. On one hand, GO as a surfactant enhances the connection between perovskite and HTM. On the other hand, GO as an insulating buffer layer can retard charge recombination in solar cells. In another work, we found that Li^+ from LiTFSI could intercalate with TiO_2 , decreasing the open-circuit voltage. In order to suppress the negative effect, we introduced spinel lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) by consuming Li^+ prior to the contact of Li^+ with TiO_2 at the interface (Figs 5d–f) [41].

Besides the corrosion from spiro-MeOTAD and additives, moisture in the atmosphere could also decompose the perovskite. We found that Al_2O_3 could serve as an insulating layer to protect perovskite from degradation in solid-state PSCs, and the devices modified with Al_2O_3 showed better stability than those without modification [14,42]. Dong and co-workers [43] used atomic layer

Figure 5 Effect of interface modification at perovskite/HTM interface on the stability of PSCs. (a–c) Perovskite degradation by TBP and interface modification by MMT: (a) UV-vis spectra before and after TBP treatment; (b) UV-vis absorption of TiO_2 /perovskite films with and without MMT modification before and after TBP treatment; (c) J - V characteristics of devices with and without MMT modification. Reprinted with permission from Ref. [39], Copyright 2015, the Royal Society of Chemistry. (d–f) Voltage decrease with Li-TFSI content increase and interface modification by LTO: (d) V_{oc} characteristics with different Li-TFSI content in the HTL; (e) a schematic of the change of the DOS of TiO_2 with more Li^+ in the HTL; (f) chemical capacitance extracted from EIS of the device with and without LTO modification. Reprinted with permission from Ref. [41], Copyright 2015, the Royal Society of Chemistry.

deposition method to deposit ultrathin Al_2O_3 layer onto HTM layer without sacrificing performance. The performance of a device stored at relative humidity (RH) ~50% without illumination for 24 days was reported to be 90% of the initial value.

Li and co-workers [44] introduced phosphonic acid amine (4-aminobutylphosphonic acid chloride, 4-AB-PACl) during perovskite film fabrication (Fig. 6a). The phosphonic ammonium additives acted as a crosslinker between neighboring grains in the film, enhancing both the device performance and stability (Figs 6b and c). The benefit of this approach may be threefold: 1) the cations from additives at the interface could enhance the adhesion of the perovskite with the oxide substrate, 2) such cations could also act as growth controlling or directing agents, through hydrogen bonding of the $-\text{PO}(\text{OH})_2$ and $-\text{NH}_3^+$, and 3) the cations could passivate the surface, making the perovskite material immune towards moisture.

Interfacial modification at the interface of perovskite/HTM could also benefit the charge transfer process. In a recent report, Cha and co-workers [45] facilitated the hole transfer from MAPbI_3 to HTM layer through introducing valence band (VB)-tuned $\text{MAPbBr}_{3-x}\text{I}_x$ quantum dots (QDs) at the interface. They found that when the VB edge of $\text{MAPbBr}_{3-x}\text{I}_x$ QDs was located below that of

MAPbI_3 perovskite, and the hole transfer from the MAPbI_3 perovskite film to the HTM layer was hindered, hence the PCE decreased. In contrast, when the VB edge of $\text{MAPbBr}_{3-x}\text{I}_x$ QDs located between the VB edge of MAPbI_3 perovskite film and the highest occupied molecular orbital (HOMO) of HTM layer, the hole transfer from the MAPbI_3 perovskite film to the HTM layer was improved, leading to significant improvements of FF, short-circuit photocurrent and PCE. In another work, Chen and co-workers [46] demonstrated that PbI_2 phase could be formed in perovskite grain boundaries and at the interface between perovskite and HTM layer by releasing the organic species during annealing. The self-induced formation of PbI_2 served as a passivation layer to reduce carrier recombination in the film, as well as in the interface between perovskite and HTM.

INVERTED-STRUCTURED PSCs

Interface engineering at the HTM/perovskite interface

The current works on interface engineering at HTM/perovskite interface mainly focus on improving the conductivity of HTM and stability issue related to the intrinsic instability of perovskite, and reaction between HTM and perovskite.

Figure 6 (a) Schematic illustration of two neighbouring grain structures crosslinked by butylphosphonic acid 4-ammonium chloride (4-ABPA). (b) Stability test of unsealed heterojunction solar cells, with devices stored in ambient air at ~55% humidity in the dark, and measured under 10% full sun intensity. (c) Evolution of encapsulated device performance measured under 10% full sun intensity during ageing at 85 °C in the dark. Reprinted with permission from Ref. [44], Copyright 2015, Nature Publishing Group.

When perovskite were firstly introduced into inverted solar cells, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) were widely studied, due to its tunable conductivity and high optical transmittance in the visible light wavelength range [47]. However, considering the mismatch between the work function of PEDOT:PSS (−5.2 to −4.9 eV) and the VB level of MAPbI₃ (−5.4 eV), PEDOT:PSS is not an ideal hole transport layer for inverted PSCs. Through film doping, the work function of PEDOT:PSS could be tuned. Lim and co-workers [48] demonstrated the doping of a perfluorinated ionomer (PFI) into PEDOT:PSS film to form a PFI-rich surface. The surface work function could be increased from −4.9 to −5.4 eV, while the V_{oc} soared from 0.835 V to 0.982 V.

The acidity of PEDOT:PSS solution often leads to the reaction with basic methyl amine groups in the structure of organometal trihalide perovskites. In addition, the PSS part is hygroscopic, increasing the instability issue, since perovskite is highly sensitive to moisture. Considering the

above drawbacks, the alternatives to PEDOT:PSS were developed.

Nickel oxide is a suitable choice to substitute PEDOT:PSS, because of its high work function and good stability. Jeng and co-workers [49] first pioneered the utilization of NiO_x in PSCs. They constructed NiO_x/perovskite/PCBM structure to achieve higher voltages. However, due to the limited conductivity of NiO_x, the performance was restricted by the poor FF. Doping has been proved as an effective method to increase the conductivity. Jen and co-workers [50,51] demonstrated solution processed and low-temperature combustion methods to prepare copper doped NiO_x. Cu is selected as a dopant due to its unique electronic and structural effects. A high electrical conductivity as high as $1.25 \times 10^{-3} \text{ S cm}^{-1}$ was achieved for Cu-doped NiO_x, much higher than the pristine NiO_x ($2.2 \times 10^{-6} \text{ S cm}^{-1}$), resulting in an impressive PCE of 17.74% (Figs 7a and b).

Besides Cu doping, Li is another effective doping cont-

Figure 7 Doping to increase conductivity of NiO_x films in inverted PSCs. (a, b) Cu doping: (a) *I-V* curves of pristine NiO_x and Cu:NiO_x measured by c-AFM, (b) *J-V* curves of PSCs based on PEDOT:PSS, NiO_x, and Cu:NiO_x hole transporting layers. Reprinted with permission from Ref. [50], Copyright 2015, Wiley Weinheim. (c and d) Li doping: (c) comparison of the *I-V* curves of NiO and Li_{0.05}Mg_{0.15}Ni_{0.8}O films deposited on FTO glass obtained by SPM measurements; (d) *J-V* curves of solar cells based on different combinations of charge extraction layers. Reprinted with permission from Ref. [52], Copyright 2015, American Association for Advancement Science (AAAS).

ents to improve the conductivity of NiO_x films. Chen and co-workers [52] improved the conductivity of NiO_x films to $2.32 \times 10^{-3} \text{ S cm}^{-1}$ by Li⁺ doping, 12 times higher than NiO_x (Fig. 7c). Moreover, Mg²⁺ was also introduced into the LiNiO_x material to adjust the VB, and thereby to enhance the hole extraction efficiency. Finally, they achieved a PCE over 15% with an aperture area >1 cm², with the device structure as NiMgLiO/perovskite/PCBM/TiNbO_x. They also introduced a thin meso-Al₂O₃ layer (90 nm) onto the ultrathin NiO compact layer. Al₂O₃ could passivate the FTO/perovskite interface, as well as block the shunt paths between NiO and PCBM [53].

Interface engineering at the perovskite/ETM interface

The interface engineering at the perovskite/ETM interface is beneficial for the following aspects: 1) blocking hole transfer, 2) reducing energy barrier for charge transfer, and 3) improving stability.

Firstly, in order to block hole transfer between PCBM and metal electrode, bathocuproine (BCP), ZnO and tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane

(3TPYMB) were used [54–56]. They could block hole transport and facilitate electron collection for their deep HOMO energy level, reducing the charge recombination in PSCs. The HOMO level or valence band maximum (VBM) are located at −7.0, −6.4, and −6.8 eV for BCP, ZnO, and 3TPYMB, respectively.

Secondly, for charge transfer, between an n-type semiconductor and metal electrode, Schottky barrier (non Ohmic contact) could be formed when the conduction band of semiconductor is higher than metal work function, leading to potential loss and lower V_{oc} . In order to address these issues, interfacial layers are used to decrease the work function of metals. The underlying mechanism of work function tuning by interfacial layer has been studied in numerous papers. Zhou and co-workers [57] have exhibited that lower work function could be obtained by depositing a thin layer of insulating ethoxylated polyethylenimine (PEIE) or branched polyethylenimine (PEI). The intrinsic molecular dipole, caused by the ethylamine group aligned along the vertical direction to the substrate, and the surface interfacial dipole formed at the organic mol-

ecule/electrode interface, both contribute to the work function change. Zhang and co-workers [58] successfully used PEIE and poly [3-(6-trimethylammoniumhexyl) thiophene] (P3TMAHT) to improve the PCE from 8.53% to 11%–12%, by lowering the work function of Ag electrode. Similarly, LiF, 4, 7-diphenyl-1, 10-phenanthroline (BPe), rhodamine 101 zwitterion, poly[(9, 9-bis(3'-(*N,N*-dimethylamino)propyl)-2, 7-fluorene)-alt-2, 7-(9, 9-dioctylfluorene)] (PFN), dodecyltrimethylammonium bromide (DTAB), and so on, could also be used to lower the work function of metal electrode [58–63].

Shao and co-workers [64] studied the effect of PCBM ordering on the performance of inverted PSCs. The band tail caused by the energy disorder of the PCBM layer introduced redundant electronic states into the band gap. The non-equilibrium photo-generated electrons could relax down to these states, resulting in reduced quasi Fermi level splitting and a smaller V_{oc} . They used a solvent annealing process to successfully prepare an ordered PCBM layer. The V_{oc} could be increased from 1.04 to 1.13 V, while the FFs were also improved, enabling a high performance of

19.3%.

Thirdly, to improve the device stability, the utilization of n-type metal oxides has been proved a successful route for the inverted PSCs. Chen and co-workers [52] introduced TiO_x electron extraction layer with Nb^{5+} doping as an inserting layer between PCBM and metal electrode. The devices exhibited remarkable stability, with less than 10% PCE degradation when exposing the cells for 1000 h in short-circuit conditions to full sunlight. The n-type metal oxides could also be employed as a single electron extraction layer. Recently, You and co-workers [65] used ZnO nanoparticles as electron transport layer (Fig. 8a). A maximum PCE of 16.1% was achieved (Fig. 8b), together with 90% retention of the original performance after 60 days storage in air at room temperature (Fig. 8c). After that, Zhu and co-workers [66] constructed inverted PSCs with SnO_2 single layer as the electron selective contact. Due to the brilliant electron transport and barrier effect of SnO_2 , the PCE was demonstrated to be 18.8%, while the device retained over 90% of the initial value after storing in ambient with > 70% RH for 30 days.

Figure 8 (a–c) Inverted PSCs assembled from solution-processed metal oxide transport layers: (a) energy band alignment of PSCs; (b) $J-V$ curve of the champion device under one sun illumination; (c) normalized performances of ITO/PEDOT:PSS/perovskite/PCBM/Al (black) and ITO/ NiO_x /perovskite/ZnO/Al (red) structures as a function of storage time in an ambient environment (30%–50% humidity, $T=25^\circ\text{C}$). Reprinted with permission from Ref. [65], Copyright 2016, Nature Publishing Group. (d–f) Insulating tunneling contact for efficient and water-resistant inverted PSCs: (d) energy diagram illustrating the suppressed surface charge recombination by the insulating layer; (e) $J-V$ curves of the devices with different insulating tunneling contacts; (f) pictures of the devices with and without fluoro-silane layer after dipping into water for 1–2 min and 5 s, respectively. Reprinted with permission from Ref. [67], Copyright 2016, Wiley Weinheim.

Most recently, Wang and co-workers [67] inserted polystyrene (PS), Teflon, and polyvinylidene-trifluoroethylene copolymer (PVDF-TrFE) between perovskite and electron transport layer. The thin insulating layer allowed the transport of photo-generated electrons in perovskite to C_{60} through tunneling, and blocked the photo-generated holes back into perovskite, as shown in Figs 8d and e. With 1% PS used as the tunneling layer, a PCE as high as 20.3% was obtained, substantially higher than the control device (16.9%). In addition, the insulating layer could also prevent perovskite films from degradation by water (Fig. 8f).

PSCs WITH CARBON ELECTRODE

PSCs with carbon counter electrodes were first reported in 2013 by Ku and co-workers [68]. Typically, there are two main methods of implanting carbon electrodes. One is the direct printing on the as-prepared substrates with perovskite layers, which needs a low-temperature processed carbon electrodes paste [69,70]. The other is the construction of carbon electrodes based mesoscopic substrates followed by the infiltration of the perovskite materials, and the carbon layers are normally prepared with high temperature annealing [71,72]. The former architecture involves regular n-i-p structure or just TiO_2 /perovskite heterojunction before the carbon electrodes, and the latter one is generally made of a triple layer mesoscopic TiO_2 /insulating layer (ZrO_2 or Al_2O_3)/C scaffold as shown in Fig. 9a. The introduction of carbon counter electrodes provides both low cost and simple preparing techniques (screen printing or doctor-blade method). On the other hand, and, more importantly, this architecture gives great examples of achieving long-term stability, which is, to date, a widely acknowledged bottleneck for the practical application of PSCs [73,74].

There are two main interfaces in the carbon electrodes based mesoscopic PSCs, the TiO_2 /perovskite interface and the perovskite/C interface. The principles of interface modification concerning the TiO_2 /perovskite interface could be straightly applied to this architecture since they have similar structure and common problems towards charge transfer, morphology control, and stability. But one thing that might limit the direct implantation of the interface modification strategies is the unbearable high temperature for most modification materials, especially the organic molecules and polymers, during the annealing process of the carbon electrodes. Han and co-workers [75] incorporated self-assembled silane monolayer between TiO_2 and $CH_3NH_3PbI_3$ to improve the interface band align-

ment and enhanced the charge extraction, as shown in Fig. 9b. A 2-propanol solution of aminopropyltrimethoxysilane was used to immerse the whole mesoscopic substrates. The self-assembled silane monolayer was claimed to form hydrogen-bonding or electrostatic interactions between the amino groups and the perovskite framework, which created a more compact perovskite loads and increased pore filling. And the PCE was increased from 9.6% to 11.7% with a highest efficiency of 12.7%. Another effective way to increase the pore filling of perovskites is using mixed-ion materials. Mei and co-workers [71] used $(5-AVA)_x(CH_3NH_3)_{1-x}PbI_3$ instead of $CH_3NH_3PbI_3$ to achieve a more complete contact between the perovskite absorbers and the mesoscopic layers. The presence of the short-chain molecule additives with both acid and ammonium groups was proved to act as crosslinker between both the perovskite grains and the TiO_2 interface.

As for the perovskite/C interface, the main problem is the hole extraction efficiency. Since the extraction of the photo-generated holes from the perovskite absorbers entirely depends on the perovskite/C Schottky junction. Yan and co-workers [76] demonstrated that an energetic difference, resulted from the work function of the carbon layer, would induce the change from Schottky junction (multilayered graphene (MG)/perovskite, work function $WF_{MG} = 5.0$ eV) to Ohmic contact (single-layered graphene (SG)/perovskite, $WF_{SG} = 4.8$ eV). Our group systematically studied the structural formation process of the $CH_3NH_3PbI_3$ /C process by *in-situ* photoluminescence (PL) measurements, and found that the interfacial contact was dominant for hole extraction. Through solvent vapor assisted treatment during PbI_2 diffusion, a uniform perovskite layer could be formed with reduced unreacted PbI_2 block layer between $CH_3NH_3PbI_3$ and the carbon electrodes, thus significantly increasing the J_{sc} of the devices [77]. It should be noted that our *in-situ* PL monitoring technique provides direct information on the reaction kinetics, crystallization process, and structural formation, which is extremely difficult to investigate through other methods.

The importance of $CH_3NH_3PbI_3$ /C interfacial contact was also observed by Yu and co-workers [78]. They employed carbon/ CH_3NH_3I bilayer as a contact engineering in the hole-conductor layer-free cell structure. It was found that the introduction of CH_3NH_3I made the carbon films denser with efficient contact with the perovskite crystals, which optimized the $CH_3NH_3PbI_3$ /C interface and facilitated the hole transport. In addition to the direct modification of the perovskite/C interface, there could be two other ways to improve the hole extraction efficiency. A

simple method is the upgrade of carbon layer. Zhang and co-workers [79] studied the effect of carbon electrodes on the efficiencies of PSCs and found that both the thickness of carbon layer and the graphite particle size influenced the square resistance of the counter electrodes, leading to different power output. Li and co-workers [80] used carbon nanotubes/carbon composite as counter electrodes, modifying their work function and extending the charge recombination lifetime, thus resulting in an increased V_{oc} of 1 V and a PCE of 14.7%. A fully replacement of mesoscopic carbon materials has also been conducted. Alternates like thiolated nanographene and cross-stacked carbon nanotubes etc. have performed well in PSCs (Fig. 9c) [81,82]. Another method involves the introduction of interfacial layer between the perovskite and carbon layer. Wang and co-workers [72,83,84] reported the use of NiO as hole selective contact and achieved a PCE of over 15% with the mesoscopic $\text{TiO}_2/\text{Al}_2\text{O}_3/\text{NiO}/\text{carbon}$ quadruple-layer architecture (Fig. 9d). NiO, as p-type inorganic materials, has been widely used as hole transport material in the inverted PSCs. Since the mesoporous NiO layer is easy

to be prepared with NiO nanoparticles, which also shows favorable energy alignment and high stability, NiO should be a proper choice of p-type interlayer material. Moreover, NiO nanosheets also performed well in extracting holes as interlayer [85]. Other than NiO, Zhang and co-workers [86] used CuPc nanorods as hole selective layer between $\text{CH}_3\text{NH}_3\text{PbI}_3$ and carbon electrodes. The CuPc interlayer showed a better hole extraction efficiency than the doped spiro-MeOTAD, therefore boosting the efficiency to 16.1%. It is foreseeable that more hole selective interfacial layers are being explored, promoting the development of highly efficient, low-cost and super stable qualities.

CONCLUSIONS AND OUTLOOK

In this review, we comprehensively reviewed the recent progress of interface engineering for PSCs. The excellent properties of perovskite materials make it a suitable absorber layer for photo-to-electricity conversion. Thanks to amounts of efforts from researchers around the world in interface engineering, film fabrication, operation mechanism, and composition control, PSCs could even compete

Figure 9 (a) Schematic illustration of the triple-layer carbon electrode based mesoscopic solar cell. The perovskite materials are infiltrated by drop-casting from solution. Reprinted with permission from Ref. [71], Copyright 2014, AAAS. (b) Energy band diagram of the device with the organic silane SAM interface modification. Reprinted with permission from Ref. [75], Copyright 2015, American Chemical Society. (c) Cross-sectional SEM images of the cross-stacked carbon nanotubes based PSCs. Reprinted with permission from Ref. [82], Copyright 2016, the Royal Society of Chemistry. (d) Energy band diagram of carbon electrode based PSCs with NiO and CuPc as p-type interlayer [83,86].

with CdTe, CIGS, and Si solar cells. However, considering the theoretical efficiency limits and stability status, there is still a long way to go before application in reality. Interface of the PSCs is vital to carrier extraction and transport in the device, as well as device stability. The ultimate goal is to satisfy the standard stability test, such as IEC61646, 2008 and JISC8938, 1995. One of the most possible solutions is to fabricate all-inorganic structured PSCs. ETM and HTM could serve as insulation layers to protect perovskite materials. Current research results have proved the possibility to obtain stable devices. However, the stability test results under working conditions, such as under light illumination and at maximum power output point, are still insufficient. For the next stage, researchers should pay more attention to the realistic operational conditions, as opposed to “shelf stability” of devices stored in the dark and measured periodically. A deep understanding of interface properties is essential to further advance PSCs towards industry. For example, the interface could influence the typically observed *J-V* hysteresis phenomenon. However, the deep mechanism, such as the suppressed trap state on perovskite, has not been fully resolved. An appropriate interfacial layer would improve the quality of perovskite thin films with high coverage and uniformity, leading to the development of the large-area PSCs that meets the industrial standards. Moreover, the involvement of low temperature processed interface materials is essential for the development of flexible PSCs. The design of tandem solar cells requires transparent electrode selection and tunnel junction design, which also needs interface engineering. Through proper interface design, including energy level alignment, charge transfer manipulation, as well as film encapsulation, it is predictable that in the future, PSCs will finally satisfy the international criteria for a thin-film terrestrial photovoltaic modules.

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Conflict of interest The authors declare that they have no conflict of interest.

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高效率钙钛矿太阳能电池的界面修饰及其研究进展

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摘要 有机-无机杂化钙钛矿由于其优异的电学及光学性质, 成为制备太阳能电池吸光层的理想材料. 无论反式还是正式结构的钙钛矿太阳能电池, 均包含以下几个关键界面: 电极/电子传输层界面、电子传输层/钙钛矿界面、钙钛矿/空穴传输层界面、空穴传输层/电极界面. 这些界面的性质对于电池性能至关重要, 因为激子的形成、分离及复合都直接决定于这些界面. 此外, 器件的稳定性也受界面性质的影响. 因此, 界面电荷转移以及相应的界面修饰对于制备高效率、高稳定性电池器件具有重要助益. 本论文将侧重综述近期在钙钛矿电池领域关于界面修饰问题的重大突破与进展.