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Topical Review

Advantages and challenges of self-assembled monolayer as a hole-selective contact for perovskite solar cells

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Abstract

Charge-transporting layers (CTLs) are important in determining the performance and stability of perovskite solar cells (PSCs). Recently, there has been considerable use of self-assembled monolayers (SAMs) as charge-selective contacts, especially for hole-selective SAMs in inverted PSCs as well as perovskite involving tandem solar cells. The SAM-based charge-selective contact shows many advantages over traditional thin-film organic/inorganic CTLs, including reduced cost, low optical and electric loss, conformal coating on a rough substrate, simple deposition on a large-area substrate and easy modulation of energy levels, molecular dipoles and surface properties. The incorporation of various hole-selective SAMs has resulted in high-efficiency single junction and tandem solar cells. This topical review summarizes both the advantages and challenges of SAM-based charge-selective contacts, and discusses the potential direction for future studies.

Keywords: hole-selective contact, self-assembled monolayer, conformal coating, covalent bonding, perovskite solar cells

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Future perspectives

Self-assembled monolayer (SAM)-based hole-transport layers (HTLs) have become a popular option for perovskite solar cells due gto their numerous advantages. In the future, we expect that the following points can be deeply studied to advance their scalable applications. (a) The stability and degradation mechanism of SAM-based HTLs should be carefully studied, for example, under operational and damp heat conditions. High-performance SAM-based HTLs are currently mostly small molecules with simple structures. The development of polymeric or *in situ* cross-linkable SAMs may address their thermal stability weakness. (b) The microstructures of the SAM layer should be carefully studied using suitable characterization methods such as surface-sensitive optical and scanning techniques. (c) The working mechanism of SAM-based HTLs should be further explored to gain a full understanding to enable us to design more efficient SAMs. It is interesting to design new SAM molecules with unique passivation groups that concurrently passivate defects of both metal-oxide and perovskite. (d) The mainstream of SAM-based charge-transporting layers is currently HTLs. The development of n-type SAMs is also important for their popularization and device efficiency.

1. Introduction

Perovskite solar cells (PSCs) are a promising photovoltaic technology as they offer high power conversion efficiency (PCE) and low-cost potential [1–4]. Typical PSCs contain a sandwich structure, namely a perovskite-based absorber layer sandwiched between the electron-transport layers and HTLs, in between the current collection electrodes [5]. In addition to the perovskite layer, the charge-transporting layers (CTLs) are also important in determining the performance and stability of PSCs [6–11]. Traditional CTLs are thin films with thicknesses of tens to hundreds of nanometers, comprising small molecules, polymers, or inorganic metal oxides [12–16]. The optimization of these CTLs is equally important to that of the perovskite layer. The dilemma with optimizing these CTLs in solar cells is that the films should be thin to minimize resistive losses while at the same time, they should cover the entire current collector area in a contiguous and uniform manner. Meeting these requirements becomes increasingly difficult as the device area increases.

Recently, several groups have proposed the use of SAMs that are chemically anchored on transparent conductive oxide electrodes (TCOs, such as tin-doped indium oxide, ITO and fluorine-doped tin oxide, FTO) to form an ultra-thin charge-selective contact and replace traditional thin-film-based CTLs in PSCs, as shown in figure 1(a) [17–20]. The development of hole-selective SAMs is more successful due to there being more available organic hole-transporting units than electron-transporting ones [21]. The molecular structure of hole-selective SAMs typically consists of an arylamine-based hole-transporting head, an anchoring group such as carboxylic acid (–COOH) or phosphoric acid (–PO(OH)$_2$) that can chemically adsorb onto the surface of the TCO, and a linker between them to assist the self-assembly (figure 1(b)). These hole-selective SAMs are particularly suitable for the inverted-structured PSCs that place the hole-extraction layer at the light incident side [22–24]. The application of SAM-based HTLs has unique advantages of minimal parasitic absorption, low material consumption and simplified fabrication for large-area PSCs. Moreover, their conformal coating character makes them broadly useful in perovskite-based tandem solar cells [25–27]. Single-junction PSCs and perovskite-based tandem solar cells employing SAM as HTLs have achieved PCEs over 24% and 29%, respectively [23, 28].

In this topical review, we discuss both the advantages and challenges of SAM-based HTLs for application in PSCs (figure 1(c)). The advantages include low-cost material production and low material consumption, negligible optical and electronic losses in devices, easy modulation of energy levels and surface properties, conformal coating on a rough surface and uniform coating over large-area substrates. Therefore, the SAM-based HTLs are particularly suitable for tandem devices, and will facilitate large-area device fabrication. The challenges of SAM-based HTLs are their fine characterization as well as long-term stability under solar cell operation. Finally, we give our perspectives on the future direction of studies of these types of CTLs.

2. Advantages of SAM-based HTLs

2.1. Cost advantages

One of the most important merits of PSCs relative to traditional photovoltaic technologies is their cost. To compete with traditional solar cells, the cost of materials and manufacturing should be as low as possible. Among the functional layers in PSCs, the perovskite layer is already very inexpensive, while some CTLs are still expensive due to their complicated synthesis and purification [33–36]. For example, the synthesis of polymer-based CTLs (such as poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine], PTAA; poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate), PEDOT:PSS; poly(3-hexylthiophene, P3HT and poly[5,5′-bis(2-butyloctyl)-(2,2′-bithiophene)-4,4′-dicarboxylate-alt-5,5′-2,2′-bithiophene], PDCBT) requires expensive catalysts and high molecular weight requirements, in addition to the problem of batch-to-batch variations [37]. SAM-based HTLs are potentially cost-effective due to the following reasons (figure 2). First, the molecular structure of the reported high-performance SAMs is very simple. In most cases, they can be readily synthesized without using precious metal catalysts, as well as complicated reaction conditions [17, 23]. Moreover, their raw materials or intermediates are broadly available and scalable due to the fertile development of organic electronics, such as organic light-emitting diodes and organic photovoltaics. Second, the molecular structure of SAM-based HTLs typically contains a hydrophilic anchoring group, which enables convenient purification by recrystallization rather than traditional column chromatography [31]. Third, the material consumption of SAM-based HTLs is much lower than that of their traditional thin-film-based counterparts because of the largely reduced

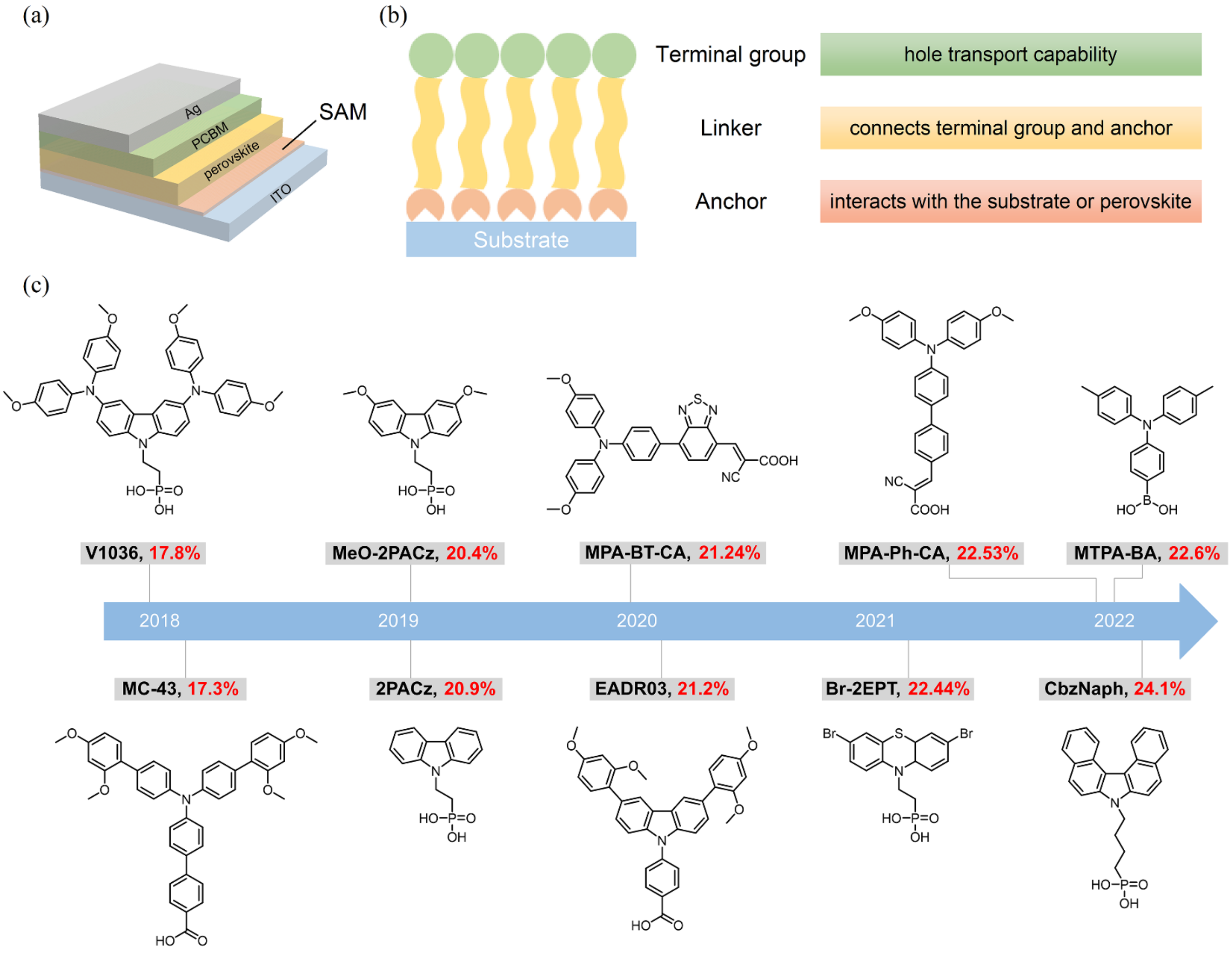

Figure 1. Application of SAM-based HTLs in PSCs. (a) Configuration of inverted structured PSCs with SAM as a hole-selective contact. (b) Schematic diagram for the molecular structure of SAMs and the roles of each segment. (c) Main progress of efficient SAM-based HTLs in single-junction PSCs (from the year 2018–2022) and their chemical structures, including V1036 [17]; MC-43 [19]; MeO-2PACz, 2PACz [18]; MPA-BT-CA [22]; EADR03 [29]; Br-2EPT [30]; MPA-Ph-CA [31]; CbzNaph [28]; MTPA-BA [32].

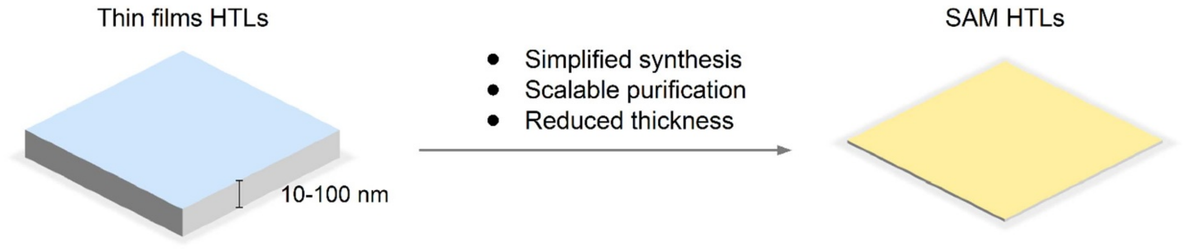

Figure 2. Illustration of cost advantages of SAM-based HTLs. Conventional thin-film HTLs require a thickness of 10–100 nm to ensure complete coverage and hole selection. SAM greatly reduces the thickness of HTL while ensuring efficient hole extraction.

layer thickness [18, 38–40]. For example, each 1 m^2 device requires about 100 g of organic HTLs if its thickness is around 100 nm (typical thickness for the well-known 2,2′,7,7′-tetrakis (N,N-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene, spiro-OMeTAD), but only several (1–5) grams of SAM will be enough for the same size device. A 100–150 MW production line will produce 2500–3000 m^2 devices every day. Therefore, the application of SAM-based HTLs in PSCs will reduce a large amount of material cost, mainly due to the reduction of layer thickness.

2.2. *Negligible optical and electric loss*

In addition to the reduced material consumption and cost, the very low thickness of SAM-based HTLs also benefits the performance of PSCs by decreasing the optical and electrical

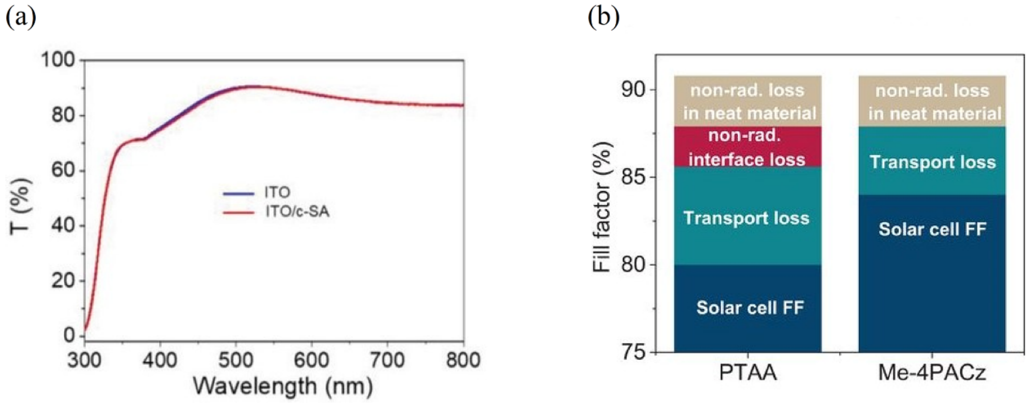

Figure 3. Low optical and electrical loss of SAM based-HTLs. (a) Transmittance spectra of c-SA fabricated on ITO glass ([20] John Wiley & Sons. [© 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim]). (b) Comparison of the loss mechanisms partition of PTAA and Me-4PACz (From [23]. Reprinted with permission from AAAS).

losses. Generally, the HTLs in PSCs should be optically transparent in the full range of the solar spectrum. For traditional thin-film-based HTLs, their band gap should be as large as possible, which largely restricted the material's design. A reduction in the band gap usually leads to inferior device performance due to parasitic absorption. In contrast, the SAMs are almost free of parasitic absorption due to their monolayer thickness features, which outperform traditional HTLs, such as nickel oxide (NiO) and PEDOT:PSS. Many papers have compared the transmittance of an ITO substrate with or without an SAM coating (figure 3(a)), confirming that such a monolayer does not cause an observable reduction in the transmittance [18, 32]. Even for some dyes that have strong absorption in the visible region, their application as SAM-based HTLs can achieve high performance of PSCs due to the thickness reduction effect [22, 31].

Another prerequisite for high-performance HTLs is that they should be highly electrically conductive to ensure low resistive loss. For traditional thin-film-based HTLs, this low resistive loss is realized by incorporating a dopant or reducing the thickness of the film [41–44]. The doping has caused severe stability issues for PSCs, while the reduction in film thickness for common HTLs raises a concern about pinhole generation [38]. The latter will increase leakage current and decrease device performance. The SAM-based HTLs were thin enough to overcome the resistive loss. On the other hand, the compactness of the SAM layer has yet to be confirmed, though several groups have tried to enhance it by optimizing anchoring groups, linkers or charge-extraction groups [31, 32, 45]. However, due to the high open-circuit voltage (V_{OC}) and fill factor (FF) performance of SAM-based PSCs, the current leakage and interfacial recombination around the SAM-based interface should be very low, as presented in figure 3(b). The Levine group used transient surface photo-voltage to investigate the charge transfer rates and electron trapping at buried interfaces in SAM-based PSCs. They found that the SAM maintains excellent selectivity to enable faster transfer rates and lower trap density, providing a reasonable explanation for the record efficiency of 29.2% in perovskite/silicon tandems [46].

2.3. Convenient modulation of energy levels

Matched energy levels at heterojunction interfaces are critical to achieving efficient charge collection and photovoltaic performance [47–50]. Compared with traditional inorganic compounds and polymers (such as NiO, PTAA, PEDOT:PSS, P3HT and PDCBT), SAMs endow convenient molecular engineering for fine modulation of energy levels (see figure 4). The SAM molecules are generally donor–acceptor (D–A) structures consisting of a hole-transporting moiety, anchors and linkers. Each part of the molecule can be readily engineered with the desired properties. We have compared a series of anchors on the phenothiazine-based SAMs, including $–SO_3H$, –COOH and $–PO_3H_2$. These SAMs show comparable highest occupied molecular orbital (HOMO) energy levels (around −5.2 eV) but different adsorption dynamics as well as device performance [40]. A strong chemical anchoring group of $–PO_3H_2$ was found to be beneficial to the improved compactness of the monolayer. We also compare the effect on the linker, namely a conjugated one versus non-conjugated alkyls, and find that a conjugated SAM is beneficial to its intrinsic stability and allows continuous rapid charge transfer. An optimal conjugated SAM of MPA-Ph-CA achieved a decent energy level alignment and an outstanding PCE of 22.53% (certified PCE of 22.12%) [31].

Compared with the variation of anchors, the modulation of the donor moiety regulates the HOMO energy level of the molecule more efficiently. The introduction of different arylamine units allows us to realize matched band alignment with various bandgap perovskites and enhanced hole selection at the interface. Al-Ashouri *et al* found that the carbazole phosphoric acid effectively stabilizes perovskite and inhibits its halogen phase separation [23]. Moreover, the HOMO of MeO-2PACz is slightly upshifted with regard to the methyl-substituted carbazole phosphoric acid SAM (2PACz). The latter was found to be more suitable for the wide bandgap (1.68 eV) perovskite. Recently, we found that boric acid can be used as an alternative anchoring group for designing SAMs. We employed a series of arylamines to construct hole-selective materials with varying energy levels [32]. Compared with

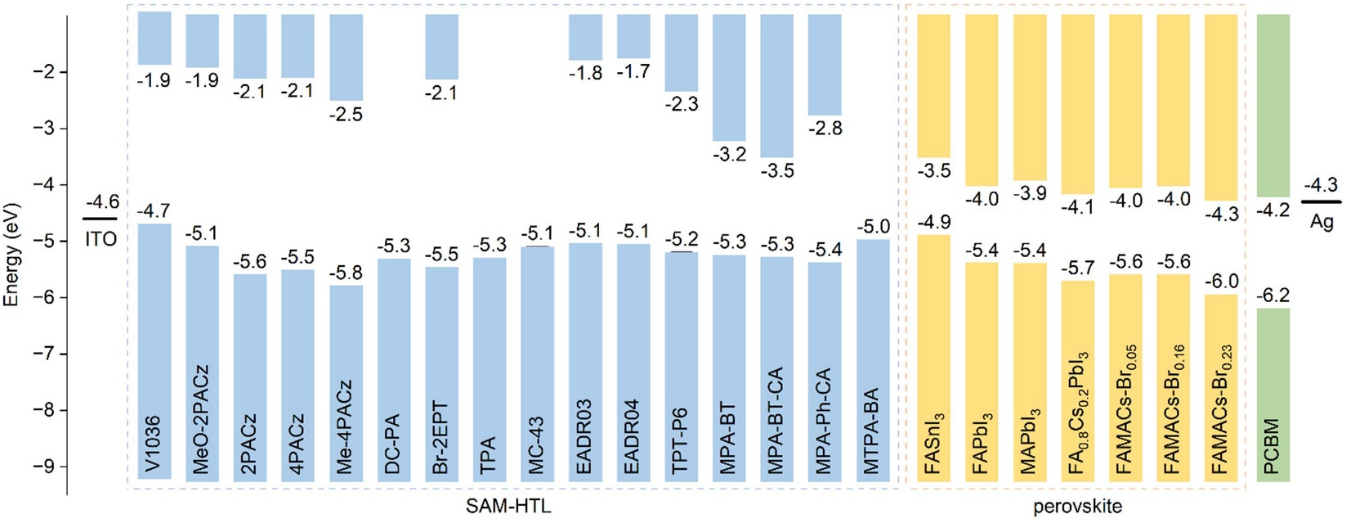

Figure 4. Convenient energy-level tuning of SAM-based HTLs, including V1036 [17]; MeO-2PACz, 2PACz, 4PACz, Me-4PACz [18, 23, 28]; DC-PA [45]; Br-2EPT [30]; TPA [19]; MC-43 [19]; EADR03, EADR04 [29]; TPT-P6 [40]; MPA-BT, MPA-BT-CA [22]; MPA-Ph-CA [31]; MTPA-BA [32]. Moreover, the FAMACs-Br$_x$ represents the perovskite components $Cs_{0.05}(FA_{1-x}MA_x)_{0.95}Pb(I_{1-x}Br_x)_3$, where x means the ratio of Br [31, 32]. Energy levels of ITO, FASnI$_3$, FAPbI$_3$, MAPbI$_3$, FA$_{0.8}$Cs$_{0.2}$PbI$_3$, PCBM and Ag were collected from the literature ([20]. John Wiley & Sons. [© 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim]. Reproduced from [21], with permission from Springer Nature).

carbazole, the introduction of triphenylamine increases the HOMO value (from −5.5 to −5.1 eV) due to the stronger electron-donating effect.

In addition to molecular energy levels, the formation of interfacial dipoles by the molecular layer also provides a versatile tool to control the work function of TCO and adjust the energy-level alignment at the interface in PSCs [51–53]. For example, when the ITO electrode is modified with a SAM having a positive dipole moment, its work function increases, which is beneficial to the hole extraction [21]. Deng *et al* reported a 2,7-position substituent carbazole DC-PA, which shows a weaker electron-donating effect than the 3,6-position substituted MeO-2PACz. Their HOMO value changed from −4.98 (DC-PA) to −5.08 eV (MeO-2PACz), and the corresponding molecular dipole increased from 0.12 to 1.64 D [45]. The Park group chose Br-2EPT as the hole-selective contact and increased the work function of the ITO interface. The resulting inverted device efficiency increased from 20.3% to 21.8% [30]. The reduced HOMO energy level induced by bromide groups minimizes the energy-band shift, thus reducing the energy loss and achieving higher V_{OC} values. Clearly, SAMs can easily regulate the band alignment by fine-tuning the molecular structure, especially the donor moiety, and therefore achieve efficient hole selection.

2.4. Convenient modification of interfaces

As shown in figures 5(a) and (b), the spin-coated SAMs are probably present in two forms, including a chemically bonded monolayer and an unabsorbed overlayer. Albrecht and co-workers found that the strong interactions between free MeO-2PACz and FAI can stabilize the black perovskite phase of FAPbI$_3$ deposited by vacuum evaporation [54]. We have demonstrated that the SAM-based HTL of MeO-2PACz is better than the commonly used HTL-like PEDOT:PSS, NiO and PTAA for stabilizing MACl-assisted one-step deposition of FAPbI$_3$ films in inverted-structured PSCs [55]. The anchors and heteroatoms in SAM molecules can also passivate the interfacial defects near the bottom part of perovskite. Ullah *et al* developed a phenothiazine-based SAM (Br-2EPT) and achieved a PCE over 22% in inverted PSCs [30]. They found that the bromine substituent in Br-2EPT forms halogen bonds with perovskite and the sulfur atoms in phenothiazine passivate the Lewis acid defects. The passivation of these defects significantly improves the charge transfer, thus enhancing efficiency while maintaining the long-term stability of devices. In addition, the passivation and interaction functions conferred by SAMs have also been used in regular structured PSCs [56], showing a broad practicability of SAMs (figure 5(c)). Due to their excellent phase stabilization and passivation capabilities, SAMs have been widely used in PSCs with different perovskite components. For example, carbazole-based SAMs have been proven to suppress light-induced halide segregation in wide-bandgap perovskite composition. Mixed halide wide-bandgap perovskite on ITO/Me-4PACz substrates achieved stable PL emission compared to PTAA (figures 5(d)–(f)) [23]. They attributed it to a combination of fast hole extraction and minimized nonradiative recombination at the hole-selective interface.

2.5. Conformal coating and compatibility with tandem solar cells

Due to the presence of strong chemical anchoring groups on the molecular structure of SAM-based HTLs, they are capable of achieving conformal coating on the surface of various rough substrates. The advantage of SAM-based HTLs makes them highly favorable for the construction of

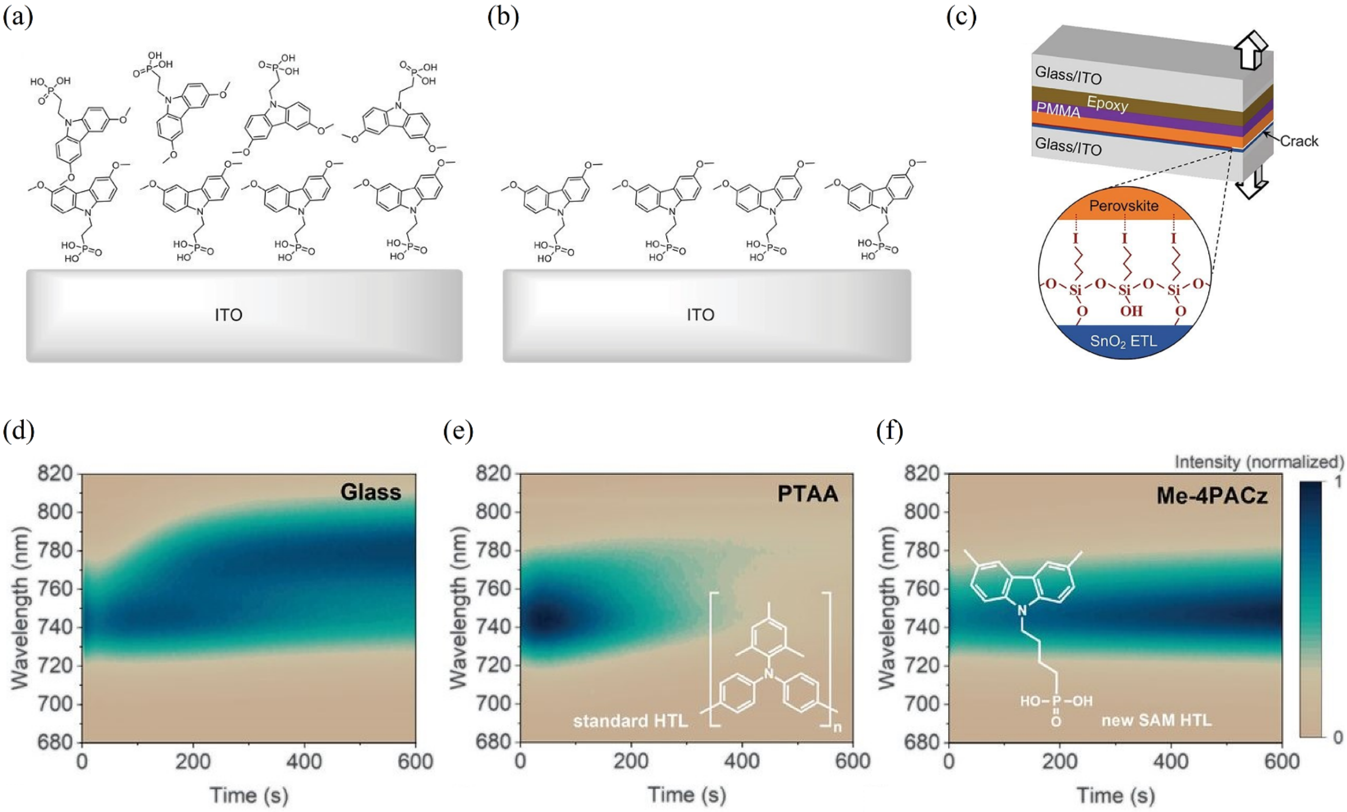

Figure 5. Modification of interfaces by SAM molecules. (a), (b) Schematic of MeO-2PACz layer deposited on ITO without/with ethanol washing ([54] John Wiley & Sons. [© 2021 The Authors. Advanced Energy Materials published by Wiley-VCH GmbH]). (c) Schematic illustration of the sandwich double-cantilever beam specimen and the magnification shows the idealized arrangement of I-SAM molecules between perovskite and SnO_2 (From [56]. Reprinted with permission from AAAS). (d)–(f) Phase stability of perovskite adsorbents on different substrates was analyzed (From [23]. Reprinted with permission from AAAS).

perovskite-involved tandem solar cells. Using this strategy (figure 6(a)), Albrecht and co-workers realized a monolithic $Cu(In,Ga)Se_2$ (CIGSe)/perovskite tandem solar cell with a certified efficiency of 23.26% on an active area of 1 cm^2 [18]. They further employed a SAM-based HTL in perovskite-silicon tandem solar cells and achieved a certified PCE of 29.15% [23]. De Wolf and co-workers chose 2PACz as a hole-selective contact and suppressed the non-radiative recombination at the buried interface, thus achieving PCE of 28.9% (figure 6(c)) and 29.3% (1 cm^2) for a monolithic perovskite/silicon solar cell [25, 57]. 2PACz can be efficiently adsorbed on the surface of ITO to enhance hole extraction at the metal-oxide and perovskite interfaces. This conformal coating of SAM also makes it more compatible with textured silicon substrates (figure 6(b)). Paetzold and co-workers utilized 2PACz as the HTL for wide bandgap PSCs in all perovskite tandem devices and achieved a PCE of up to 19.1% for an aperture area of 12.25 cm^2 [58]. Meanwhile, 2PACz can suppress halide segregation and stabilize wide-bandgap PSCs, resulting in decent operational stability for tandem devices. More importantly, SAM-based HTLs have been explored to fabricate flexible tandem solar cells. Tan groups developed a molecular bridged NiO (MB-NiO) using MeO-2PACz and 2PACz complexes. MB-NiO enables a matched band alignment and stable covalent linkage at the perovskite and substrate interfaces, resulting in a champion PCE of 24.7% for 0.049 cm^2 and 23.5% for 1.05 cm^2 for flexible all-perovskite tandems [59]. The SAM-based HTLs thus show a huge potential for achieving high-efficiency, stable tandem and flexible PSCs.

2.6. *Uniform coating over large-area substrates*

Unlike traditional thin-film coating methods, the chemical anchoring-based self-assembly process is helpful for the formation of uniform thin layers over large-area substrates. It avoids crystallization, siphoning, coffering effects and many other processes that are commonly encountered during solution-based thin-film deposition. Therefore, SAM-based HTLs are preferable for the fabrication of large-area devices. We have used SAM-based HTLs to fabricate a 36 cm^2 mini-module consisting of ten subcells connected in series [20]. The almost identical short-circuit current density (J_{SC}) and PCE of the ten subcells suggest that the uniformity of each layer in the module is quite good, indicating a high superiority of the SAM-based HTLs for PSC scale-up. Abdollahi Nejand *et al* employed 2PACz to fabricate a 12.25 cm^2 mini-module by blade coating (figures 6(d) and (e)), and the resulting all-perovskite tandem solar cells realize a PCE of 19.1% with improved operational stability [58]. Therefore, SAM has

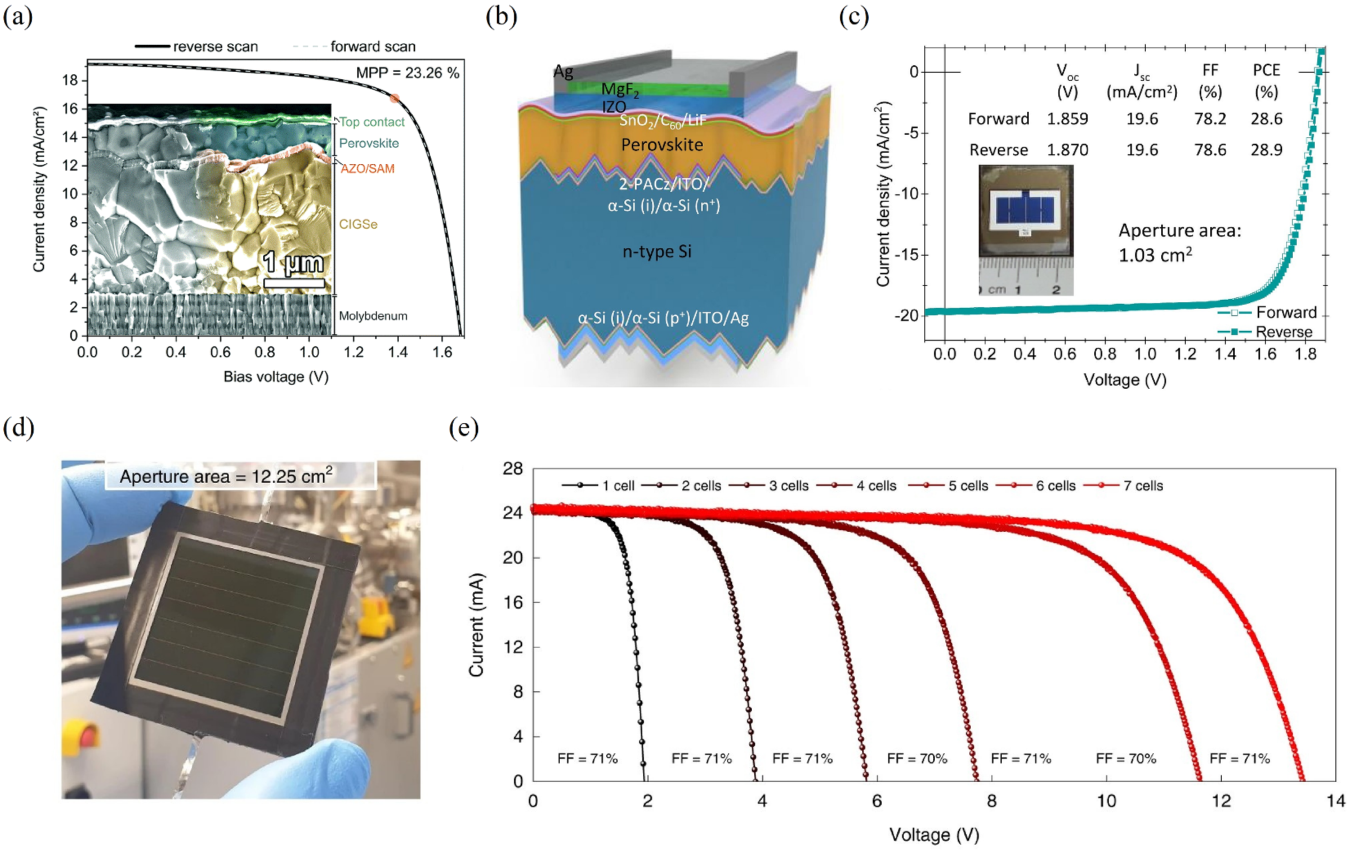

Figure 6. Conformal coating and application in tandem solar cells. (a) *J–V* curves of a monolithic CIGSe/perovskite tandem solar cell, inset: cross-section scanning electron microscopy (SEM) image of tandem cell (Reproduced from [18] with permission from the Royal Society of Chemistry). (b) Structure of the textured monolithic perovskite/Si tandem device. (c) Champion *J–V* curves of a 1.03 cm^2 tandem cell, inset: photo of the corresponding device. (b), (c) Reprinted from [25], Copyright (2021), with permission from Elsevier. (d) Front of the fabricated tandem module with an aperture area of 12.25 cm^2. (e) *J–V* curves of stepwise accumulated tandem cell stripes and respective FF. (d), (e) Reproduced from [58], with permission from Springer Nature. CC BY 4.0.

the potential to fabricate devices with a large area. For future practical manufacturing, a series of techniques could be used to realize the large-scale uniform fabrication of these monolayers, including dip coating, blade coating, slot-die coating and others. The key points to ensure high uniformity of these monolayers are creating a suitable substrate that can provide sufficient and homogeneous adsorption sites and designing efficient SAM molecules that can adsorb fast and robustly. Possible inhomogeneities such as unabsorbed SAM molecules can be removed by post-treatment, such as solvent washing. Recently, an interesting work reported that SAMs can be fabricated by vapor-phase deposition [60], which is also promising for future large-scale manufacturing.

3. Challenges of SAM-based HTLs

3.1. Characterization challenges

Since the SAM-based HTLs are mainly composed of organic small molecules and chemically adsorbed on metal oxides with very thin characteristics, a straightforward observation of their microstructure, for example, by SEM or transmission electron microscopy, is quite difficult. In most studies, researchers used x-ray photoelectron spectroscopy (XPS), atomic force microscopy and water contact-angle measurements to confirm the presence of SAM formation. Sum-frequency generation vibrational spectroscopy was applied to characterize the adsorption process as well as the interfacial molecular ordering [39, 59]. However, these characterization methods cannot reveal the real state of the monolayer on a complex surface of metal oxides. For example, it is hard to confirm the defects and continuity of the monolayers. Moreover, as the HTLs are as thin as monolayers, the charge transport process across this layer is also challenging. There are still debates on the working mechanism of these SAM-based HTLs. Some researchers deem this layer as a work function modification layer [18, 29, 56], while some others think it takes part in the charge extraction and transportation processes [19, 28, 61]. In this regard, more surface- and interface-sensitive technologies are required to fully understand the properties and working mechanisms of these SAM-based HTLs.

3.2. Stability challenges

The molecular structure of SAM-based HTLs is mostly simple and has low molecular weight. Moreover, they can absorb some sunlight in the high-energy region (UV light). Therefore, the thermal and light stability of SAM-based HTLs might be a significant concern for practical applications, especially for the SAM-based HTL in single-junction inverted PSCs, in which the SAM layer is located at the light incident side. We have tried to improve the stability of SAMs by screening different anchor groups, and found that the $–PO_3H_2$ chemisorbed onto ITO by a stronger tridentate mode compared to the bidentate mode of $–SO_3H$ and –COOH. Density functional theory (DFT) calculations show that the adsorption energy on the most stable ITO (111) surface of $–PO_3H_2$ is -2.71 eV, while $–SO_3H$ and –COOH are -2.49 and -2.15 eV, respectively [40]. ITO/TPT-P6 maintains 95% absorbance before and after solution washing, which further confirms the stronger adhesion of TPT-P6. The excellent anchoring strength is beneficial for improving the self-assembly rate, film formation quality and anchoring stability, thus promoting charge collection and inhibiting interfacial complexation. Regarding the photostability, we found that the widely used MeO-2PACz showed significant degradation after light and electrochemical tests. Therefore, we have adjusted the molecular structure by replacing the alkyl linkers with a conjugated phenylene group [31]. The conjugated structure enables an efficient charge delocalization and spatial separation of molecular HOMO and lowest unoccupied molecular orbital (LUMO) orbitals, thus stabilizing the light and electrochemical properties of the SAM. We report a series of conjugated SAM-based hole-selective contacts for efficient and stable inverted PSCs. Similarly, the Palomares group added an extra phenyl linker to the carbazole carboxylic acid (EADR04), thus realizing a higher decomposition temperature (from 180 °C to 354 °C) and thermal stability [29].

We also found that the strong acid-based anchoring group is unfavorable for the long-term stability of ITO due to acid-induced corrosion. To overcome this problem, we developed a weak boric acid group anchoring SAMs [32]. We find that the organic boric acid group is able to bond to ITO with a high adsorption energy value up to -3.62 eV. XPS further confirms the covalent linkage between ITO and boric acid, which is not susceptible to the environment and solvents. Moreover, the weak boric acid significantly reduced ITO corrosion and improved interfacial stability, maintaining satisfactory operational stability over 400 h.

4. Conclusion

In this review, we mainly summarize the progress of SAM-based HTLs in p–i–n PSCs and consider their future research direction and commercial application. Compared to other traditional CTLs, including metal oxide and polymer HTLs, SAMs exhibit special advantages in terms of low cost, negligible optical and electrical loss, convenient modulation of energy levels, and uniform and complete coverage on rough and large substrates. However, the investigation of SAMs still has several challenges, especially the limited characterization techniques and moderate stability. Moreover, we provide our own insight on future research on SAM-based perovskite photovoltaics.

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