Conjugated Polymers as Hole Transporting Materials for Solar Cells

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Abstract In principle, conjugated polymers can work as electron donors and thus as low-cost p-type organic semiconductors to transport holes in photovoltaic devices. With the booming interests in high-efficiency and low-cost solar cells to tackle global climate change and energy shortage, hole transporting materials (HTMs) based on conjugated polymers have received increasing attention in the past decade. In this perspective, recent advances in HTMs for a range of photovoltaic devices including dye-sensitized solar cells (DSSCs), perovskite solar cells (PSCs), and silicon (Si)/organic heterojunction solar cells (HSCs) are summarized and perspectives on their future development are also presented.

Keywords Conjugated polymers; Hole transporting materials; Dye-sensitized solar cells; Perovskite solar cells; Silicon/organic heterojunction solar cells

INTRODUCTION

Since Shirakawa, Heeger, and MacDiarmid discovered electrical conductivity of doped polyacetylene in 1977,[1] conjugated polymers have attracted considerable research interests. Instead of being used as pure electrical conductors, conjugated polymers have shown intriguing semiconducting characteristics and found their applications in a range of optoelectronic/electrophotonic devices that led to the award of Nobel Prize for Chemistry in 2000.[2] In particular, research efforts on employing conjugated polymers in high-efficiency, low-cost photovoltaic cells have significantly grown so as to tackle the demand for inexpensive renewable energy with low carbon footprint. These newly designed thin-film solar cells generally do not work on traditional space charge layers found in crystalline silicon (or other inorganic semiconductors) solar cells and are more compatible to industrial printing techniques. For instance, conjugated polymers can replace conventional liquid electrolytes in dye-sensitized solar cells (DSSCs) (Fig. 1a) or directly work in perovskite solar cells (PSCs) (Fig. 1b) and silicon (Si)/organic heterojunction solar cells (HSCs) (Fig. 1c) as efficient hole transporting materials (HTMs). The main function of these HTMs is to effectively extract and promptly transport holes that are generated by excited light harvesters, realizing efficient separation of electrons and holes for an improved photo-to-electricity conversion efficiency (PCE). In addition, HTMs may also work as a barrier to prevent the ingress of moisture and/or oxygen and thus protect the photo-active layer from ambient-induced degradation, improving the long-term stability of the device. As the solubility, band structure and energy level of conjugated polymers can be conveniently tuned by changing their side chains, functional groups and/or degree of polymerization via organic synthesis, it is possible to have made-to-measure polymeric HTMS for specific applications as demonstrated in bulk heterojunction (BHJ) solar cells and light-emitting diodes.[3−6] To date, while some excellent works have systematically reviewed the use of organic and/or inorganic HTMs in photovoltaic devices of DSSCs,[7,8] PSCs,[9−11] Si/organic HSCs,[12] and bulk heterojunction solar cells,[13,14] there is no work that specifically elaborates on the recent progress of conjugated polymers as HTMs in DSSCs, PSCs, and Si/organic HSCs. In this research highlight, we will focus on some widely-used conjugated polymers including poly(3,4-ethylenedioxythiophene) (PEDOT), poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS) (Fig. 1d) and evaluate their performance as HTMs in the above-mentioned devices. Meanwhile, the current limitations and future prospects of these polymeric HTMs are also presented.

CONJUGATED POLYMERS AS HTMS IN DSSCS

In 1991, O'regan and Grätzel first prepared a nanostructured DSSC using a liquid electrolyte containing triiodide/iodide ([I−]/[I3−]) redox couples and reported a PCE of 7.1%−7.9% under a simulated AM 1.5G illumination.[15] While the PCE of DSSCs based on liquid electrolytes later exceeded 13%,[16−19] electrolyte leakage and volatilization remained as a major obstacle for their secure and large-scale industrialization. In order to overcome these limitations, solid-state organic and inorganic HTMs were therefore investigated,[20−24] where con-
jugated polymers of PPy, PANI, P3AT and PEDOT have been successfully demonstrated as efficient HTMs in DSSCs.

**PPy-based HTMs**

As a heterocyclic conjugated polymer, PPy is a strong electron donor and thus can work as an excellent HTM. Additionally, its good stability and environmental benignity are highly desirable. Yanagida and co-workers first employed photoelectrodeposited PPy as the HTM in DSSCs in 1997 and reported a PCE of 0.1% under a light intensity of 22 mW·cm$^{-2}$.[21]

They further replaced the Pt counter electrode with a viscous carbon-based counter electrode to give a more homogeneous filling in the void of PPy and consequently achieved a better electric contact between PPy and the counter electrode,[24] leading to an improved PCE of 0.62% under a low light intensity of 10 mW·cm$^{-2}$.[24]

Cervini et al. later found that the intercalation of Li$^+$ ions during the photoelectropolymerization of PPy enhanced its ionic conductivity and thus led to a dramatic increase in the PCE of the device from 0.06% to nearly 1% over one-month illumination under a light intensity of 17 mW·cm$^{-2}$.[25]

While PPy did perform as the HTM in DSSCs, the performances of PPy-based cells were far from satisfaction. In situ photoelectrochemical polymerization of pyrrole is generally used to give uniform deposition of PPy onto the dye-anchored TiO$_2$ nanoporous photoanode for a better pore filling, but as PPy is an intrinsically strong light absorber in the visible spectrum, the deposited dense PPy layer severely competes with the sensitizer molecules for light capture, leading to a decreased number of photoexcited dye molecules and thus a lower photocurrent.

**PANI-based HTMs**

Apart from PPy, PANI is one of the most investigated conducting polymers over years. It can work as a p-type semiconductor of good environmental stability both in doped and neutral states.[26,27] Tan et al. first used PANI as a possible HTM in DSSCs by spin-coating a PANI solution directly onto a dyed TiO$_2$ film.[28]

However, possibly due to the poor pore filling and/or energy level mismatch, these devices only showed an open-circuit voltage ($V_{oc}$) of 310 mV and a short-circuit current density ($J_{sc}$) of 21 μA·cm$^{-2}$ under a light intensity of 110 mW·cm$^{-2}$.[28] They then optimized the conductivity, film formation property, and cluster size of PANI,[29] achieving a PCE of 0.10% under a simulated illumination at 100 mW·cm$^{-2}$. Further doping PANI with 4-dodecylbenzenesulfonic acid and addition of Li and 4-tert-butylpyridine (t-BP) helped to form a hole conducting PANI matrix in the device,[30] significantly boosting the PCE to 1.15% under 100 mW·cm$^{-2}$ light intensity. On the other hand, in order to improve pore filling of the HTM, in situ photoelectropoly-
merization and plasma-enhanced polymerization of aniline were developed to facilitate the penetration of PANI into nanopores of the TiO$_2$ mesoporous film, resulting in enhanced PCEs of 0.8% and 0.68% under light intensities of 14.5 and 100 mW·cm$^{-2}$, respectively.$^{[31,32]}$ Recently, Duan et al. hybridized PANI with ($^{13}$C$^3$)-incorporated polyethylene oxide) as a mixed HTM in DSSCs and obtained an impressive PCE of 6.1% under 100 mW·cm$^{-2}$ light intensity,$^{[33]}$ rendering a new route to further increase the photovoltaic performance of DSSCs based on PANI HTMs.

**Thiophene-based Conjugated Polymers as HTMs**

P3ATs are popular conjugated polymers due to their relatively high hole mobility, good solubility, and high environmental stability.$^{[34]}$ Among them, poly(3-octylthiophene) (P3HT) and poly(3-octylthiophene) (P3OT) are the most widely used. Gebeeyehu et al. spin-coated P3OT as the HTM in DSSCs and reported a PCE of 0.15% under white light illumination at 60 mW·cm$^{-2}$.$^{[35]}$ Similarly, Kudo et al. used P3HT as the HTM and achieved a PCE of 0.24% under a light intensity of 100 mW·cm$^{-2}$.$^{[36]}$ The relatively poor performances of DSSCs using P3OT and P3HT HTMs were mainly ascribed to the limited mobility of charge carriers in polythiophene and non-optimized pore filling of these polymeric HTMs into mesoporous TiO$_2$ films.

In order to enhance the network impregnation of the P3OT,$^{[37]}$ Sanchez and co-workers optimized nanoporous TiO$_2$ films by tuning their architecture, porosity, and layer thickness. When combining the P3OT HTM with the optimized TiO$_2$ nanoporous electrode, they obtained a stable PCE of 1.30% under white light illumination at 100 mW·cm$^{-2}$.$^{[38]}$ Among them, poly(3-hexylthiophene) (P3HT) and poly(3-octylthiophene) (P3OT) are the most widely used. Thyagaraj et al. spin-coated P3OT as the HTM in DSSCs and reported a PCE of 0.15% under white light illumination at 60 mW·cm$^{-2}$.$^{[35]}$ Similarly, Kudo et al. used P3HT as the HTM and achieved a PCE of 0.24% under a light intensity of 100 mW·cm$^{-2}$.$^{[36]}$ The relatively poor performances of DSSCs using P3OT and P3HT HTMs were mainly ascribed to the limited mobility of charge carriers in polythiophene and non-optimized pore filling of these polymeric HTMs into mesoporous TiO$_2$ films.

In 2010, Huang et al. blended a fullerene derivative (6,6)-phenyl-C$_6$B$_{14}$-butyric acid methyl ester, PCBM with P3HT and used this mixture as the HTM in DSSCs.$^{[44]}$ The bulk hetero-junction of P3HT/PCBM effectively functioned as the HTM layer and a PCE of 3.09% was achieved under a simulated illumination at 100 mW·cm$^{-2}$. In addition, an all-conjugated diblock copolymer, poly(2,5-dihexyloxy-p-phenylene)-b-poly(3-hexylthiophene) (PPP-b-P3HT),$^{[45]}$ was also tested as the HTM (Fig. 2a). The device exhibited a promising PCE of 4.65% under AM 1.5G illumination, implying that block copolymers can work as excellent HTMs even in the absence of expensive fullerene moieties. Up till now, the most efficient DSSCs based on P3HT HTMs were fabricated by Clément and coworkers through selecting an organic dye (D102) and a highly regioregular P3HT with narrow dispersity.$^{[46]}$ The device showed a PCE of 4.78% under AM 1.5G illumination, which was even higher than that of DSSCs based on the widely used HTM of 2,2′,7,7′-tetrakis(N,N-dilauroylmethoxyphenylamine)9,9′-spirobi fluorene (spiro-OMeTAD).

**PEDOT-based HTMs**

Due to its multiple merits such as high charge transport property, remarkable stability at room temperature and high transparency in the visible spectrum,$^{[47]}$ PEDOT is deemed as an ideal HTM for DSSCs. In 2004, Yanagida’s group used in situ photo-electrochemically polymerized PEDOT as the HTM and obtained a PCE of 0.53% under AM 1.5G illumination.$^{[48]}$ This type of device was soon improved to show a PCE of 1.26% when an amphiphilic Ru dye (Z-907) was used.$^{[49]}$ Further doping PEDOT with different counteranions (i.e. TFSI$^-$, CF$_3$SO$_3$-, IO$_4^-$, and BF$_2^-$) could increase the PCE up to 2.85%.$^{[50]}$ In addition, judicious selection of an organic indoline dye (D149) as the sensitizer was shown to facilitate the in situ polymerization of 2,2′-bis(3,4-ethylenedioxythiophene)$^{[51]}$ leading to a lower photoelectron recombination, a better polymer penetration for hole transportation and an impressive PCE of 6.1% under AM 1.5G illumination. Such an excellent result promoted applications of organic donor–acceptor (D-n-A) sensitizers in combination with PEDOT-based HTMs and high PCEs of 5.54% and 7.11% (Fig. 2b) under simulated AM1.5G illuminations have been reported with D-n-A type sensitizers of LEG4 and DPP07, respectively.$^{[52,53]}$
POLYMERS AS HTMS IN PSCS

While different conjugated polymers have been validated as possible HTMs in DSSCs, their performances were relatively poor and the PCEs were well below those of DSSCs based on liquid electrolytes. This was an unsolved dilemma until the debut of PSCs. As demonstrated in the previous section, the performance of conjugated polymer HTMs is highly dependent on the type of photosensitizer and therefore a wise selection of the sensitizer is a prerequisite to a high PCE for devices based on conjugated polymer HTMs. Fortunately, lead perovskites seem to be perfect teammates for these polymeric HTMs. To date, the highest certified PCE of PSCs was 25.2% and the device worked with the expensive, hygroscopic and heat-sensitive HTM of spiro-OMeTAD. In comparison, PCEs of over 20% can be reliably obtained by replacing spiro-OMeTAD with low-cost, air-stable conjugated polymer HTMs. Currently, conjugated polymers are attractive HTM candidates in PSCs and based on polytriarylamine, P3HT, and PEDOT:PSS are mostly studied.

Polytriarylamine-based HTMs

Polyarylamines are an important class of hole conducting materials in organic photovoltaics due to their high affinities to holes induced by triarylamine units. In particular, poly-(bis(4-pheny1)(2,4,6-trimethylphenyl)amine) (PTAA) has been regarded as one of the most efficient polymeric hole conductors due to its high hole mobility \( (10^{-2} - 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}) \), low thermal degradation rate and strong interaction with perovskites.

In 2013, PSCs based on a three-dimensional nanocomposite of mesoporous TiO\(_2\)/CH\(_3\)NH\(_2\)PbI\(_2\) and PTAA HTM were shown to have a maximum PCE of 12.0% under standard AM 1.5G illumination. In contrast, the PCE of devices based on spiro-OMeTAD was only 8.4%. The superior performance obtained with PTAA was attributed to the lower series resistance and the larger work function, resulting in improved fill factor (FF) and \( V_{oc} \) respectively. Later, Seok and co-workers continued to use PTAA HTM and obtained certified PCEs of 16.2% and 17.9% when perovskites prepared by a solvent engineering technology or from mixed cations of methyl amonium (MA) and formamidinium (FA) were selected as the photoactive layer, respectively.

Bi et al. employed the non-wettability of PTAA to promote high-aspect-ratio crystalline perovskite grain growth on the PTAA HTM and demonstrated a high stable PCE of 18.3% under 1 sun illumination. In addition, further increasing crystalline grains of organolead trihalide perovskites and decreasing the concentration of deep-level defects pushed similar device to show stable PCEs of 20.2% and 22.1%, respectively.

Apart from working as an efficient HTM, PTAA has been used in a variety of special PSCs aiming for long-term stability. In principle, the presence of amine nitrogen in the backbone of PTAA prevents delocalization of electrons between adjacent phenyl units and limits the effective conjugation length, leading to a better anti-oxidative ability and thus a higher stability in air. For instance, with PTAA as the HTM and choline chloride as the defect passivation layer, a \( p-i-n \)-structured PSC device achieved a certified PCE of 20.6% ± 0.5% and retained almost 100% of its initial PCE after stored under ambient conditions for over one month. Moreover, Seok et al. used an entire range of MAPb\(_{1-x}\)Br\(_x\)\(_2\) (\( x = 0.2 \)) as the light harvester and PTAA as the HTM to prepare colorful PSCs. The corresponding cells exhibited a maximum PCE of 12.3% under standard AM 1.5G illumination and did not change significantly after 20 days of stability testing. Likewise, Liu et al. also chose PTAA as the HTM to prepare all-inorganic CsPbI\(_3\) PSCs and obtained a PCE of 15.07% that maintained 92% of its initial value after two-month storage under ambient conditions. In addition, Jost et al. used a hole transport conformal bilayer based on PTAA/NiO\(_x\) and achieved an optimal PCE of 21.6% in perovskite/CIGSe tandem devices that was stable over 10 min of maximum power point tracking. The introduction of PTAA was found to improve the \( V_{oc} \) and FF of tandem solar cells when compared to devices only with the NiO\(_x\) HTM. Quite recently, Kim et al. prepared PTAA derivatives (1F-PTAA, and 2F-PTAA) by sequential fluorination and applied them as HTMs in PSCs. The HOMO energy levels of both PTAA derivatives were significantly decreased to approach the valance band maximum of the perovskite, resulting in an obvious increase in \( V_{oc}\). Impressively, PSCs using (FA\(_\text{PbI_3}\))\(_{0.85}\)(MAPbBr\(_3\))\(_{0.15}\) as the sensitizer and 1F-PTAA as the HTM achieved a stabilized PCE of 21.2% at the maximum power point and a high \( V_{oc}\) of 1.14 V.

P3HT-based HTMs

Similar to scenarios in DSSCs, P3HT is an interesting HTM candidate in PSCs. In earlier works, the performance of P3HT-based HTM was unsatisfactory, mainly due to its relatively low hole mobility \( (3 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}) \) and fast non-radiative recombination at the perovskite/P3HT interface. For instance, Hodes et al. first used P3HT as the HTM in conjunction with CH\(_3\)NH\(_2\)PbBr\(_3\), and only obtained a low PCE of 0.52%. Later on, Snaith et al. complemented the P3HT HTM with a perovskite-sensitized TiO\(_2\) layer functionalized with a fullerene self-assembled monolayer (C\(_{60}\)SAM) and considerably improved the PCE to 6.7%. Furthermore, PCEs of 10.8%, 13.6% and 13.7% were obtained for PSCs with P3HT-based HTMs by using highly concentrated CH\(_3\)NH\(_2\)PbI\(_3\)Cl perovskite precursors, atomic-layer-deposited compact TiO\(_2\) film, and high-efficiency sequentially vapor-grown CH\(_3\)NH\(_2\)PbI\(_3\) film, respectively.

Despite these improvements, the low hole mobility of P3HT remained as an issue and the performances of PSCs with P3HT HTMs were generally inferior to those based on Li-doped spiro-OMeTAD. Such a problem can be partly solved by doping P3HT with LiTFSI and/or t-BP. When Li-TFSI and t-BP were added in the P3HT HTM, a doubled PCE of the device (from 6.5% to 13.5%) was observed. Alternatively, hybridizing P3HT with carbon nanomaterials is another viable way to enhance charge mobility of the HTM layer. For example, PCEs of 6.45%, 8.3%, and 14.58% were reported for PSCs using P3HT-based HTMs with additions of multi-walled carbon nanotubes, bamboo-structured carbon nanotubes and graphene, respectively. Snaith’s group used a single-walled carbon nanotubes/P3HT composite HTM in combination with hydrophobic PMMA to simultaneously enhance hole percolation and device stability (Fig. 3a). The resulting device exhibited a maximum PCE of 15.3% and excellent stability with no significant change in color after 96 h of exposure to air at 80 °C (Fig. 3b), proving the great potential of polymeric HTMs in the future development of

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P3HT/SWNT-PMMA as HTL
Perovskite absorber

Fig. 3 (a) Schematic illustration of the perovskite solar cell with P3HT/SWNTs-PMMA as the HTM; (b) Photo illustrating the visible degradation of the perovskite layer. The color shifts from almost black to yellow for all organic HTLs except for the films covered with PMMA only or a composite of carbon nanotubes and PMMA; (c) The structure of an n-i-p perovskite solar cell based on a DHA using P3HT as the hole-transport material; (d) Stability tests of control and DHA devices at 85% relative humidity without encapsulation and under 1 sun illumination upon encapsulation (Reprinted with permission from Ref. [82]; Copyright (2014) American Chemical Society) (Reprinted with permission from Ref. [56]; Copyright (2019) Nature).

PEDOT:PSS-based HTMs

Recently, PEDOT:PSS has been widely employed as the HTM in inverted PSCs due to its excellent conductivity, high transparency, and high work function. In 2013, Chen and co-workers first used PEDOT:PSS as the HTM to prepare inverted planar heterojunction PSCs, obtaining a PCE of 3.9% under simulated AM 1.5G illumination when PCBM was used as the electron transport layer. The PCE of such a device was quickly improved to 10% on glass substrates and over 6% on flexible polymer substrates by sandwiching solution-processed CH$_3$NH$_3$PbI$_3$Cl$_x$ perovskite absorbers between PEDOT:PSS and PCBM in inverted planar PSCs. Further improvement in the crystallinity and grain size of the perovskite layer by proposed solvent annealing, moisture-assisted film growth and single-step spin-coating method led to PSCs with PCEs of 15.6%, 17.1%, and 18.1%, respectively. In order to further enhance the efficiency and stability of inverted PSCs, Wu et al. used the synergistic effect of H$_2$O and DMF to prepare a high-quality 500-nm-thick perovskite film with large grains and a very smooth surface. The corresponding inverted cell with the PEDOT:PSS HTM featured an impressive PCE of 20.1% and an improved stability in inert and ambient atmospheres with appropriate encapsulation. Unfortunately, the hydrophilic and acidic nature of PEDOT:PSS still destabilize the interface between ITO and PEDOT:PSS. A MoO$_3$ layer was then introduced between ITO and PEDOT:PSS to address the issue. It not only increased the hole transport properties from perovskite to the ITO electrode, but also completely separated ITO and PEDOT:PSS. As the result, a maximum PCE of 14.87% was achieved and the device still retained 93% of its initial PCE after stored under ambient conditions in the dark for 10 days. By further optimizing thickness of the MoO$_3$ layer, a PCE of 18.8% was achieved. Besides MoO$_3$, a thin layer of perylene could also be used to separate ITO and PEDOT:PSS, leading to stable PSCs that showed a maximum PCE of 17.06% and 69.9% retention of the initial PCE after 200 h under ambient conditions even without encapsulation.
POLYMERS AS HTMS IN SILICON (SI)/ORGANIC HSCS

Aside from DSSCs and PSCs, HSCs combine advantages of high-efficiency crystalline Si cells with low-cost organic semiconductors and provide a practical option for cost-effective photovoltaics. Typically, conjugated polymers are prevailing HTMs in Si/organic HSCs due to their facile processability and high stability.

In an early seminal work, Lewis and co-workers constructed an n-Si/poly-(CH\(_2\))\(_3\)Si-cyclooctatetraene solar cell and obtained a PCE of 1.5% under a low light intensity of 9 mW·cm\(^{-2}\). More importantly, the device showed a \(V_{oc}\) of 0.64 V, which approached the theoretical limit, and greatly exceeded the values found in conventional n-Si/metal HSCs. Since then, conducting polymers-based Si/organic HSCs have attracted wide attentions and different conjugated polymers, such as PEDOT:PSS, PANI and P3HT have been studied. PEDOT:PSS and PANI were first selected as the p-type semiconductor in Si/organic HSCs and PCEs of 2.1% and 3.55% were accordingly achieved under the light intensity of 100 mW·cm\(^{-2}\), respectively. Later, Sturm et al. optimized such devices by selecting P3HT as the HTM and obtained a high PCE of 10.1% under simulated illumination at 100 mW·cm\(^{-2}\). This improvement was attributed to the large conduction band-LUMO barrier (~0.8 eV) and a negligible valence band–HOMO barrier at the silicon/P3HT interface, resulting in a high \(V_{oc}\) of 0.59 V and a large \(J_{sc}\) of 29 mA·cm\(^{-2}\).

Owing to its outstanding electrical and optoelectronic properties, the combination of PEDOT:PSS with n-Si might offer a better photovoltaic performance. As severe interfacial recombination may take place at the Si/PEDOT:PSS interface, inserting a capping layer between Si and PEDOT:PSS to passivate interface can well improve the PCE of HSCs. For example, Yu et al. introduced an intermediate 1,1-bis(di-p-tolyaminophenyl)cyclohexane (TAPC) layer into the silicon nanowires/PEDOT:PSS interface (Fig. 4a) to suppress interfacial carrier recombination, yielding a PCE of 13.01%. Sun and colleagues introduced a thin layer of MoO\(_3\) film on the PEDOT:PSS layer (Fig. 4b) and improved the PCE of the device from 12.2% to 13.8%. Such an increase in the PCE was attributed to the high work function MoO\(_3\) and anti-reflecting effects of the MoO\(_3\) layer to boost \(J_{sc}\) and \(V_{oc}\) simultaneously. Alternatively, a silane (3-glycidoxypropyltrimethoxysilane) layer was incorporated into PEDOT:PSS layer to hinder the surface recombination and increase adhesion between PEDOT:PSS and nanostructured Si, resulting in a record \(V_{oc}\) of 640 mV and a PCE of 14.1%. Cui’s group further combined a capping Cui layer deposited on the PEDOT:PSS film with tetramethylammonium hydroxide (TMAH) pretreatment of Si substrate (Fig. 4c) to obtain a stable PCE of over 14.3%. Additionally, in order to optimize the interfacial recombination between Si and the rear electrode, fluorine-doped titanium oxide film and magnesium oxide film were used as an electron-selective passivating layer in textured-Si/Al HSCs pushing PCEs of HSCs to 15.10% and 15.5%, respectively.

With another strategy, He et al. found that post-coating a water-insoluble phthalic acid ester, diethyl phthalate (DEP),

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Fig. 4 (a) Fabricated device schematic with insets showing the structure of pristine silicon nanowires on the left and the morphology of spun-casted TAPC on the right; (b) Device structure of the MoO\(_3\)/Ag Grids/PEDOT:PSS/n-Si/Liq/Al hybrid solar cells; (c) Device configuration of the Si/PEDOT:PSS heterojunction solar cell with a Cul capping layer (Reprinted with permission from Ref. [97]; Copyright (2013) American Chemical Society) (Reprinted with permission from Ref. [99]; Copyright (2014) Wiley) (Reprinted with permission from Ref. [101]; Copyright (2016) American Chemical Society).

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onto the PEDOT:PSS layer fostered a fully conformal contact between the PEDOT:PSS layer and textured-Si pyramids, achieving a stable PCE of 16.2% and up to 90% retention of this value after stored under 85% humidity for 300 h without additional encapsulation. Quite recently, a bilayer PEDOT:PSS film composed of a high-conductivity PEDOT:PSS in the top layer and a high-adhesion PEDOT:PSS in the bottom layer was shown to achieve a conformal contact and effective carrier collection on textured Si surface (Fig. 5).[205] With the aid of a layer of fullerene derivative (CPTA) chemically bonded to the Si substrate, the PCE of the device was improved from 12.6% to over 16.7%.

**Fig. 5** (a) Configuration of a PEDOT:PSS/n-Si heterojunction device; (b) SEM image of an HA-PEDOT:PSS film on n-Si pyramids. Scale bar: 500 nm; (c) Schematic illustration of the molecular packing arrangements for HA-PEDOT:PSS and HC-PEDOT:PSS films on an n-Si substrate; (d) Chemical bonding of CPTA to an n-Si substrate (Reprinted with permission from Ref. [205]; Copyright (2018) American Chemical Society).

**SUMMARY AND PROSPECT**

In conclusion, conjugated polymers have been successfully applied in DSSCs, PSCs, and Si/organic HSCs as hole transporting materials. PTAA-based HTMs are widely used in highly efficient PSCs with long-term stability, outperforming other polymeric HTMs. However, PTAA is significantly more expensive and its application is particularly challenging in large-area commercial productions. In comparison, HTMs of P3AT and PEDOT:PSS are more cost-effective and further improvements in their device performance would put them on a more competitive position. Overall, by optimizing the nature of the polymeric HTMs and the interface between HTMs and other components, the PCEs of corresponding devices have been gradually approaching some of benchmark values set by other prevailing HTMs such as spiro-OMeTAD.

While these achievements are highly desirable, there are some issues unsolved before their potential industrial applications. First of all, the PCE of these devices seems to be highly dependent on a suitable selection of the polymeric HTM and the dye/perovskite and a further understanding on such a phenomenon would clarify the effects of parameters such as energy level alignment and surface morphology on the photovoltaic performance. Second, interfacial engineering needs to be fully considered in optimizing interfaces adjacent to the polymeric HTM and thus promoting hole transportation while reducing unwanted charge recombination. Last but not least, the cost of the polymeric HTM should be further reduced while its stability requires additional improvements for potential large-scale applications. With all these measures, HTMs based on conjugated polymers would certainly find their indispensable position in commercializing low-cost photovoltaic devices.

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