



Recent progress in electron transport bilayer for efficient and low-cost perovskite solar cells: a review

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Abstract

Today, organic–inorganic perovskite hybrid solar cells are especially attracted by the energy industries to design and develop new-generation photovoltaic devices. They are the most promising materials for high PCE and cheap solar cells. They can also solve the current energy demand of society and the global crisis. Over the past few years, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has increased rapidly from 3.8 to 24.2%. However, the review focuses on the recent development of the electron transport layer due to the most important parameter perovskite solar cells to enhance the performance and stability of the device. These summaries discuss device architectures, single and double electron transport (ETL) layers, ETL optimization, and perovskite active layer interface for efficient perovskite solar cells. Moreover, the doping effects on the charge transport layer/window layers of PSCs were reviewed. In addition, the performance and stability issues for organic–inorganic halide perovskite solar cells are discussed here. Finally, future research on bilayer ETL and the perovskite active layer interface was also offered.

Keywords Perovskite · Electron transport · Active layer · Doping · Mesoporous

Introduction

Organic–inorganic perovskite hybrid solar cells are particularly attracted by the energy industries to design and develop new generation photovoltaic systems with the aim to address the current affordable and green energy demand of society. As a result, organic–inorganic hybrid perovskites are the promising materials for high power conversion efficiency (PCE) and low-cost solar cells. In recent years, the PCE of perovskite solar cells (PSCs) has quickly increased from 3.8 to 24.2% [1, 2]. To date, the highest efficient organic–inorganic hybrid perovskite solar cells shows the power conversion efficiency of over 20%. These materials have excellent optoelectronic properties such as

strong light absorption with a low band gap, long charge carrier lifetimes, high carrier mobility, and long diffusion length. Beside this, an excellent charge transport properties make them very attractive [3, 4]. The crystal structures of the perovskite has a general formula of AMX_3 as shown in Fig. 1 where “A” is an organic cation such as methylammonium (MA^+) or formamidinium (FA^+), “M” is a metal cation (e.g., Pb^{2+} or Sn^{2+}) and “X” stands for the halide anion (e.g., Br^- , I^- , Cl^-) or a mixture of them.

In 2006 and 2009, the first organometallic lead halide perovskites, methyl-ammonium lead iodide and bromide ($MAPbBr_3$ and $MAPbI_3$) were used as sensitizers in dye-sensitized solar cells by Miyasaka and co-workers, and their devices showed a 3.13% and 3.81% efficiency, respectively [1, 6]. Moreover, in 2011, Park’s and co-workers demonstrated a highly efficient quantum-dot-sensitized solar cell with a power conversion efficiency of 6.5% using $CH_3NH_3PbI_3$ quantum dots (QD) deposited on a nanocrystalline TiO_2 surface. However, their device had poor stability which was degraded 80% of the sensitizer within 10 min [7]. The liquid electrolyte of the dye synthesized solar cell with the TiO_2 electron transport layer was replaced by the solid hole transport layer to enhance the conversion efficiency by Spiro-OMeTAD

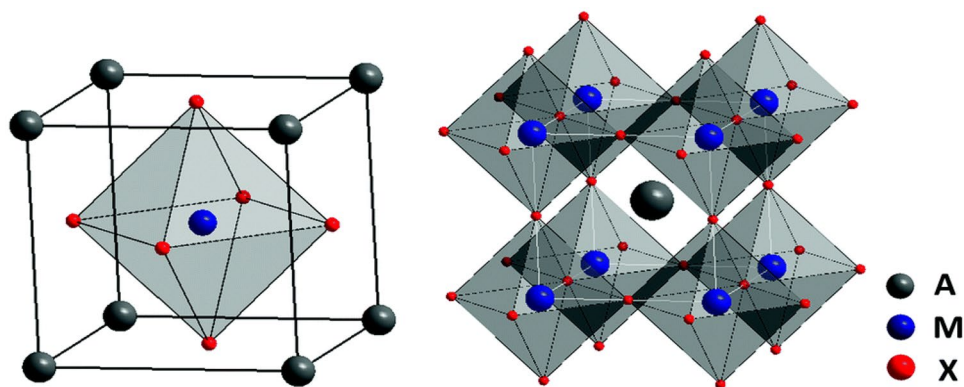
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Fig. 1 Cubic perovskite crystal structures with the general formula of AMX_3 [adopted from Ref. 5]



(2,2',7',7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene) and achieved 9.7% PCE [8]. In 2013, Liu et al. reported planar heterojunction perovskite solar cells using both vapor deposition and solution treatment method and TiO_2 used as an electron transport layer. The power conversion efficiency of both methods was reached by 15.4% and 8.6% without nanostructure and by replacing the traditional one-step solution method [9]. The first introduced organic–inorganic halide perovskite $CH_3NH_3PbCl_{3-x}I_x$ was used as a light absorber and showed good stability in the air compared to conventional $CH_3NH_3PbI_3$. Therefore, efficiency has been improved by adopting Al_2O_3 nanoporous as scaffolding instead of TiO_2 from 7.6 to 10.9% [10]. Researchers have been working to design new efficient perovskite photon-absorbing materials, to improve the synthesis mechanism/methods, and manipulate the electronic structure of the photon-absorbing perovskite active layer to harness the highest possible portion of visible light. To date, the electron and hole transport layers have received considerable attention due to their impact on the photogenerated carrier collection efficiency of the cell. Moreover, the interface between the photon absorbing layer, electron transport layer (ETL), and hole transport layer (HTL) has to be given due attention to improve the photogenerated charge carrier collection efficiency [11, 12]. The major function of the ETL is to carry/transport photogenerated electrons from the perovskite photon active layer to the contact electrode, and the layer effectively blocks the holes from migrating to the counter electrode. These phenomena enhance the charge carrier separation kinetics due to the kind of ETL used and reduce electron–hole recombination at the interface [13, 14]. Therefore, this review article briefly discusses the recent progress in the PSCs, the single and double ETLs and the kinetics of photogenerated carriers at the interface of PSCs. A special attention is given for metal oxide layers reporting for the last 5 years. Moreover, the effects of doping on PSC charge transport/window layers were examined. Additionally, the current advancement of PSCs on the stability and

performance of inorganic–organic halide perovskite solar cells has been discussed as well.

Perovskite solar cells

Device architectures

The typical device architectures of perovskite solar cells are analogous to solid state dye sensitized solar cells (ss-DSSCs). The basic architectures of perovskite solar cells are mesoporous, planar and inverted planar, which are shown in Fig. 2.

Mesoporous perovskite solar cells

Mesoporous materials have been studied and used extensively due to their high porosity and large specific surface area. Its high surface area enables to harvest more density of photons and reduces recombination rate and improving the charge collection the efficiency of the solar cell device. Mesoscopic perovskite solar cells were introduced by using methyl-ammonium lead iodide $CH_3NH_3PbI_3$ and bromide $CH_3NH_3PbBr_3$ to serve as sensitizer on mesoporous TiO_2 , and PCE of achieved 3.82% and 3.13 with an organic liquid electrolyte [6]. Kim et al. studied perovskite mesoscopic solar cells using the solid hole transportation layer (Spiro-OMeTAD), TiO_2 as ETL, and to prevent rapid degradation of performance due to the dissolution of the perovskite material into the liquid electrolyte [8]. However, the most commonly used perovskite mesoscopic solar cells uses TiO_2 compact thin film as ETL and mesoporous such as TiO_2 , ZnO, SiO_2 , Al_2O_3 , and ZrO_2 . To date, above 20% power conversion efficiency for mesoscopic perovskite solar cells has been reported [18, 20, 21, 25, 27]. Moreover, perovskite solar cells prepared from various mesoporous perovskite photon-absorbing layers with different ETL are summarized in Table 1.

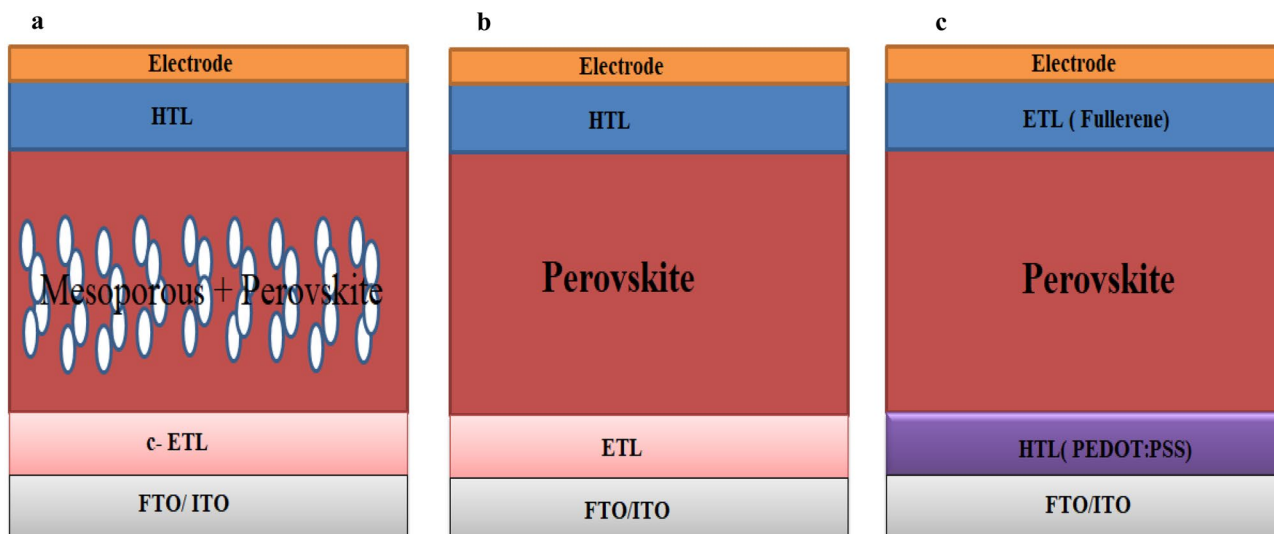


Fig. 2 Various device architectures of perovskite solar cells: **a** mesoporous, **b** planar, and **c** inverted planar device [adopted from Ref. 15]

Scaffold material in perovskite solar cells In perovskite solar cells, a scaffold material serves as a support layer and frame, but it cannot transfer electrons into the cells. These materials have wide band gaps and a conduction band border that is substantially higher than the perovskite layer's conduction band, preventing smooth electron injection into both SiO_2 and ZrO_2 . As a result, the excited electron spends more time in the perovskite layer's conduction band. Various research groups have reported employing TiO_2 , ZnO , Al_2O_3 , Nb_2O_5 , SiO_2 , and ZrO_2 as scaffold materials in perovskite solar cells, with a PCE of around

10% SiO_2 [32], Al_2O_3 [33, 34], and ZrO_2 [35]. The Al_2O_3 interlayer was introduced between the Li-SnO_2 ($\text{Li}^+\text{-SnO}_2$) ETL and the $\text{CH}_3\text{NH}_3\text{PbI}_3$ layer using the low-temperature process sol-gel technique, and the Al_2O_3 layer covers the top of the perovskite layer. The device's performance and stability have been improved, and the power conversion efficiency has been boosted to 10%. The fill factor drops due to a weak interface contact between the perovskite layer and the carbon counter electrode. At the interface between the ETL and the perovskite layers, the Al_2O_3 layer in the device reduces electron-hole recombination, resulting in

Table 1 The performances of mesoscopic perovskite solar cells with ETL layer

Perovskite active layers	ETLs	V_{oc} (V)	J_{sc} (mA/cm ²)	PCE (%)	Ref
MAPbI_3 ($\text{CH}_3\text{NH}_3\text{PbI}_3$)	c- TiO_2 /mp- TiO_2	1.04	20.44	15.51	[16]
$(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Cs}_{0.05}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ (CsFAMA)	mp- TiO_2 -Ba(OH) ₂	1.09	20.81	17.53	[17]
MAPbI_3 ($\text{CH}_3\text{NH}_3\text{PbI}_3$)	Mg TiO_3 /mp- TiO_2 with hole-conductor-free	0.95	14.05	22.62	[18]
MAPbI_3 ($\text{CH}_3\text{NH}_3\text{PbI}_3$)	Bi-Mg-SnO ₂ /mp-SnO ₂	1.112	22.80	19.12	[19]
MAPbI_3 ($\text{CH}_3\text{NH}_3\text{PbI}_3$)	c- TiO_2 /mp-Sb doped SnO ₂	1.10	23.81	20.1	[20]
$(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Cs}_{0.05}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ (CsFAMA)	c-SnO ₂ /mp-Sc ³⁺ doped brookite TiO ₂	1.145	23.63	21.75	[21]
$\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ (GO or m GO)	c- TiO_2 / mp- TiO_2	0.85/0.93	20.49/ 24.43	8.96/13.25	[22]
MAPbI_3 ($\text{CH}_3\text{NH}_3\text{PbI}_3$)	PET/ITO/SnO ₂ /meso-TiO ₂	1.036 ± 0.011	20.70 ± 0.28	14.07 ± 0.58 (14.8)	[23]
MAPbI_3 ($\text{CH}_3\text{NH}_3\text{PbI}_3$)	c- TiO_2 /mp- TiO_2	1.059	19.62	15.12	[24]
$(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$	c- TiO_2 /GQD-x/mp- TiO_2	1.08	24.92	20.45	[25]
MAPbI_3 ($\text{CH}_3\text{NH}_3\text{PbI}_3$)	O-mp- TiO_2	1.13	22.4	19.7	[26]
$\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Br}_x$	c- TiO_2 /mp- TiO_2	1.141	23.42	20.43	[27]
$\text{MAPbI}_3\text{Cl}_{3-x}$	mp- Al_2O_3 /mp- TiO_2	1.069	20.78	16.84	[28]
$\text{CH}_3\text{NH}_3\text{PbI}_{2.6}\text{Cl}_{0.4}$	c- TiO_2 /mp- TiO_2	1.045	20.1	12	[29]
$\text{MAPbI}_{3-x}\text{Br}_x$	Bi- TiO_2 /H ₃ PW ₁₂ O ₄₀ nH ₂ O/mp- TiO_2	1.03	23.55	18.20	[30]
$(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$	c-Nb ₂ O ₅ /m-Nb ₂ O ₅	1.04	23.2	17.4	[31]

better perovskite solar cells. Also, a good way to increase the short-circuit current density [36]. Xiong et al. Reported carbon-based perovskite solar cells with hole-conductor free associate degreed incorporation of an Al_2O_3 layer modifies the interface between the electron transport layer and perovskite active layer. It also reduced the energy loss at the interface between ETL and perovskite layer and counter conductor leads, preventing the electron–hole recombination. This serves as an excellent insulating layer to separate the cathode and anode [37]. Niu et al. used aluminum as a post-modification material to investigate the stability of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and the sensitized film under moisture and sunlight. Al_2O_3 improved the stability and efficiency of perovskite solar cells by protecting them from moisture and UV

deterioration. In addition, it reduces electron–hole recombination at the TiO_2 surface and spiro-OMeTAD shown in Fig. 3a. The device post-modified by Al_2O_3 has shown more brilliant stability than that without modification when exposed to moisture [33]. Similarly, Dong et al. introduced an interface modification method using ultra-thin Al_2O_3 layers to improve the ambient stability of perovskite solar cells. The results showed that the ambient stability of the prepared perovskite solar cell was greatly improved without a significant reduction in efficiency. Moreover, they used molecular structure modeling to explain the degradation mechanisms of organic/inorganic hybrid structures and they found that the hydrogen bonding interactions between the inorganic PbI_3 unit and organic CH_3NH_3 unit play an important role

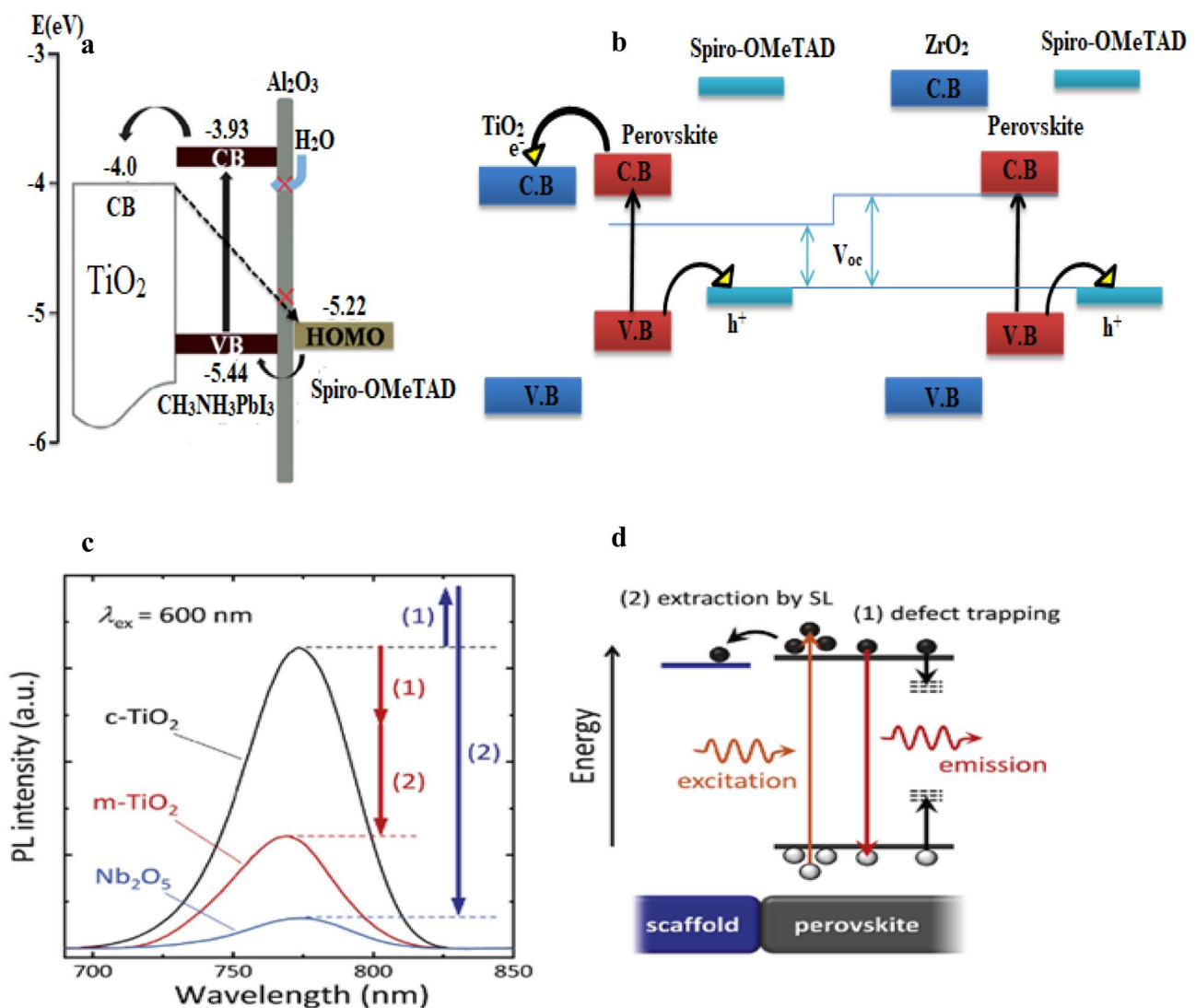


Fig. 3 Schematic description of **a** energy level diagrams of the device with post-modification by Al_2O_3 , **b** the energy levels in the two solar cell interfaces and a model for the charge separation processes, **c** PL spectra of the perovskite films on Nb_2O_5 (blue), mesoporous- TiO_2

(red), and compact- TiO_2 (black) scaffold layers. **d** Schematic illustration, representing relaxation of photoexcited carriers in perovskite film [adopted from Ref. 33, 35, and 38]

in determining the stability of $\text{CH}_3\text{NH}_3\text{PbI}_3$ [34]. Bi et al. examined synthesized ZrO_2 and TiO_2 as mesoporous layers for perovskite thin film solar cells using two-step and one-step deposition processes. When using the two-step and one-step approaches to compare the power conversion efficiency of ZnO_2 and TiO_2 . The two-step technique for ZnO_2 (PCE: 10.8% for ZnO_2)-based solar cells outperforms both the one-step and two-step techniques for TiO_2 -based solar cells (PCE: 9.8% for TiO_2). As a result, the electron lifetime in solar cells based on ZrO_2 is longer than in solar cells based on TiO_2 at the same voltage shown in Fig. 3b [35]. Inami et al. has been reported Nb_2O_5 as a scaffold layer (SL) and compared the electron-extraction capability at the perovskite/ Nb_2O_5 and the perovskite/m- TiO_2 interface. The photoluminescence spectroscopy results revealed the higher electron-extraction capability at the perovskite/ Nb_2O_5 interface than the perovskite/m- TiO_2 interface shown in Fig. 3c. They also proposed the relaxation of photoexcited carriers in perovskite film shown in Fig. 3d.

Also, it was revealed not only to functions as the efficient electron transport layer but also to facilitate crystallization of the overlying perovskite film, both of which are important factors for high-performance perovskite solar cells. It was also found that the perovskite layer on Nb_2O_5 shows fewer pinhole defects than the perovskite/m- TiO_2 film. Therefore, the superior optoelectronic properties, better photovoltaic performance, and stability of mesoporous the perovskite solar cells [38]. In 2019, Tomulescu et al. revealed mesoporous TiO_2 layers with a high-roughness reticulated structure that can be applied to large surfaces using a spray-coating approach in the ambient atmosphere. These layers are used as a mesoporous scaffold in PSCs with small and large active areas up to 1 cm^2 , and the average power conversation efficiency was 10 to 12% higher than devices with a spin-coated smooth surface mesoporous scaffold. As a result, reducing charge losses within the solar cell's most resistive component layer was beneficial for perovskite settlement, allowing the deposition of a thicker perovskite and increasing the length of the interface between TiO_2 and perovskite, as well as improving photogenerated charge collection and reducing hysteresis [29]. In 2020, Daneshvare Asl et al. published a thin film containing mesoporous nanoparticles, nanorods, and nanobranched nanorods as a scaffold for perovskite solar cells. However, due to better optical properties, nanobranched nanorods outperformed nanoparticles and nanorods in photovoltaic performance, demonstrating excellent electron transport properties and desired light-harvesting performance, which are desirable features for increasing the efficiency of perovskite solar cells [39]. Overall, scaffold materials play an important role in perovskite solar cells because they protect recombination electrons from the electron transport layer interface and the perovskite absorber layer interface/electrode, as well as providing

a higher electron extraction capability from the perovskite absorber layer interface to the ETL interface. Additionally, the fracture and pinhole between the FTO substrate and the perovskite interface/electrode were minimized.

Planar perovskite solar cells

In typical planar perovskite solar cells, the perovskite active layer is the sandwich between the electron transport layer and hole transport layer, forming both interfaces contacting with charge transport layers. They are hot topic currently due to their unique advantages such as low cost, high efficiency, easy processing, and low-temperature process [40]. James M. Ball et al. proposed a low-temperature solution process technique for preparing planar thin-film architectural perovskite solar cells with power conversion efficiencies of about 12.3% [41]. Traditional planar PSCs based on compact TiO_2 , ZnO , or SnO_2 as well as inverted planar perovskite solar cells are included in the structure of planar perovskite solar cells [42]. Each layer in planar perovskite solar cells has its own advantage for improving the device's performance [43]. As a result, there are a variety of methods for improving the performance of planar perovskite solar cells, including perovskite crystalline regulation [44], the design of new perovskite components [45], surface morphology control [46], and modification of the charge carriers transport layers and perovskite absorber layer interface [47]. Furthermore, numerous studies have reported on the performance of planar perovskite solar cells using different techniques. Recently, Zhu et al. used K and Cl ions at the ETL/perovskite interface to passivation the ETL/perovskite contact and grain boundaries, demonstrating an increase in open-circuit voltage from 1.077 to 1.137 V and a 22.2% increase in power conversion efficiency using SnO_2 -KCl composite ETL. As a result, defect passivation in the trap density will be lowered, and nonradiative recombination loss will be reduced [48]. Lee Y and co-workers prepared SnO_2 electron transport layer by using low-temperature atomic layer deposition (ALD) with excellent extraction and hole-blocking ability. They found that the surface passivation of SnO_2 is very crucial to reduce charge recombination at the perovskite and ETL interface because of this the prepared planar perovskite solar cells exhibit high reproducibility, stability, and power conversion efficiency of 20% [49].

They also recommended that the chemical and electrical properties of the ALD SnO_2 film were strongly associated with deposition and postannealing temperature. However, the charge collection from perovskite to SnO_2 can be less influenced by the downward shift of conduction band maximum and Fermi level of SnO_2 film but, strongly affected by crystallinity and proper surface passivation of the SnO_2 layer. The microstructures from scanning electron microscopy of the ALD SnO_2 films deposited at $120 \text{ }^\circ\text{C}$ and the

complete perovskite device are displayed in Fig. 4 [49]. Similarly, Subbiah et al. used ALD method and prepared amorphous Nb_2O_5 with and without an interfacial passivation layer of phenyl-C61-butyric acid methyl ester (PCBM) as ETLs. The device performance exhibits superior behavior in terms of hysteresis, scan rate dependency, and stability associated with ETL–perovskite interactions and ALD- Nb_2O_5 fabricated using a PCBM interfacial layer. Their results also confirmed that Nb_2O_5 suitable for evaporated perovskite absorbers with power conversion efficiency about 15.4% [50]. The combined solution-processed and spin-coating techniques was employed to prepare Nb_2O_5 thin films by Shen et al. They used the prepared Nb_2O_5 thin films for both mesoscopic and planar types of perovskite solar cells. They obtained the power conversion efficiencies about 17.4 for mesoscopic while as high as 19.2% from planar perovskite solar cells. Their results also revealed that the thickness of Nb_2O_5 thin films affects the quality of the device by reducing the charge recombination rate [31]. Another promising composite-controlled SnO_2 nanostructure was reported by Singh and co-workers. The results showed that the ground and compact composite SnO_2 nanostructure formed a robust ETL having efficient carrier transport properties; accordingly, carrier recombination between the ETL and mixed perovskite was inhibited. Moreover, the power conversion efficiency of the device was reported about 21.09% with excellent long-term stability [51]. Tang et al. fabricated hysteresis-free PSCs device based on a hybrid ETL of SnO_2

and carbon nanotubes (CNTs) which was prepared by simple thermal decomposing.

In this case, the addition of CNTs significantly improved the conductivity of SnO_2 films and reduced the trap-state density of SnO_2 films, which benefits carrier transfer from the perovskite layer to the cathode. As a result, a high efficiency of 20.33% was achieved in the hysteresis-free PSC device, which showed 13.58% enhancement compared with the conventional device [52]. In 2016, Anaraki et al. used a low-temperature solution process to prepare excellent SnO_2 ETL to fabricate highly efficient planar PSCs and achieved the power conversion efficiency of close to 21%. Moreover, the stability of the device retains more than 82% of the initial efficiency over 60 h [53]. Luo et al. came up with a strategy to reduce nonradiative recombination for the inverted devices, based on a simple solution-processed secondary growth technique. This approach produced a wider band gap top layer and a more n-type perovskite film, which mitigates nonradiative recombination, leading to an increase in *open-circuit voltage* (V_{oc}) by up to 100 mV. They achieved a high V_{oc} of 1.21 V without sacrificing photocurrent, corresponding to a voltage deficit of 0.41 V at a band gap of 1.62 eV. This improvement led to a stabilized power output approaching 21% at the maximum power point [54]. Currently, planar perovskite solar cells show relatively high PCEs between 20 and 21.4% [55]. However, the mesoporous perovskite solar cells have greater PCEs than planar [56, 57]. Therefore, planar PSCs do not reach world records yet; researchers are

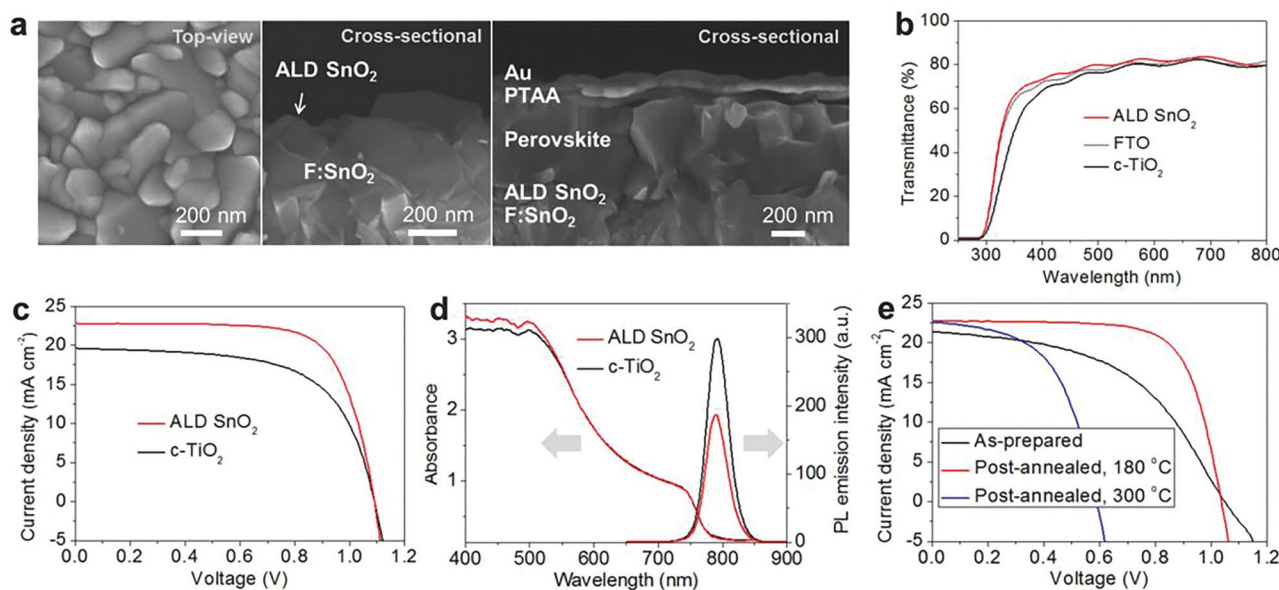


Fig. 4 Planar-type perovskite solar cells with ALD SnO_2 ETLs. **a** SEM images of the ALD SnO_2 films and the complete perovskite solar cell. **b** Transmittance of the ALD SnO_2 , FTO, and c- TiO_2 films. **c** J - V curves with SnO_2 and c- TiO_2 films. **d** Absorbance and photolu-

minescence emission spectra of the perovskite films formed on the ALD SnO_2 and c- TiO_2 substrates. **e** J - V curve change according to postannealing of ALD SnO_2 films [adopted from Ref. 50]

less willing to switch from meso to planar, even though it is industrially more preferable [58].

Electron transport materials in perovskite solar cells

The electron transport layer in perovskite solar cells prevents the hole from migrating to the counter electrode by capturing and conveying the excited photogenerated electron from the perovskite absorber layer [59]. In addition, to improve carrier separation and reduce electron–hole recombination at the interface. ETL features such as charge mobility, energy level alignment, trap states, interface, and surface morphology all contribute to the efficiency of perovskite solar cells. As a result, high charge mobility ETL is the most important factor for effective perovskite solar cells, as it leads to efficient charge collection and transportation while suppressing charge recombination at the interface [60, 61]. Another element that improves the efficiency of perovskite solar cells is energy level alignment. When ETL is better aligned with the perovskite absorber layers, electron extraction and transportation become much easier. This means increasing the device's short-current density (J_{sc}), fill factor (FF), and open-circuit voltage (V_{oc}). Other significant factors in defining high-efficiency photovoltaic perovskite solar cells are charge extraction, transport, and recombination at the interface. One of the most critical factors in the ETL is trap states, which influence charge extraction and transport, indicating a high recombination rate at the interface. One technique to improve the electron transport layer and the performance of photovoltaic perovskite solar cells is to use interface engineering. The device performance can also be improved by improving the ETL's surface morphologies. As a result, all elements play a role in determining the device's attributes [61, 62]. Figure 5 a shows some charge carrier injection (i and iii), transport and collection (ii), and recombination

mechanisms (iv and v) within PSCs. These kinetic processes and influences factor have a significant impact on device performance. The schematic representation of the PSC work mechanism and a review of the parameters that influence the function of ETLs are extremely useful in determining the underlying causes of PSC solar performance improvement through ETL optimization [63]. To obtain efficient photovoltaic perovskite solar cells, the presence of ETL is crucial requirement to extract and transport excited the photogenerated electron from perovskite absorber layer to its counter electrodes [64].

Although different groups claimed to obtain power conversion efficiency of more than 13% for ETL free devices but still dominant efficiency and stability of the devices with the incorporation of electron transport layers [65, 66]. Therefore, the selection of proper electron transport layers must fulfill the following criteria such as good electron mobility, wide band gap, and compatible energy level [67]. Wide band gap inorganic semiconductors are excellent ETL candidates and have been utilized extensively to fabricate highly efficient PSCs due to their low cost and considerable charge mobility. So far, binary and ternary metallic oxides and some chalcogenides materials used as ETLs. Their band structures and electron mobilities are listed in Fig. 5b [68]. Among them, until now TiO_2 is a widely used ETL and higher PCE than others, but the electron recombination rates are very high due to low conductivity and electron mobility which are unfavorable for electron collection and transport properties. Moreover, they have defects such as oxygen vacancies and metal interstitials at the surface and grain boundaries that make less efficient and poor stability PSCs [69]. As a result, different studies have been conducted in order to improve the performance and stability of photovoltaic perovskite solar cells. To improve the qualities of electron transport layers, there are two essential aspects (ETLs). The first method involves doping additional elements into the ETL structure,

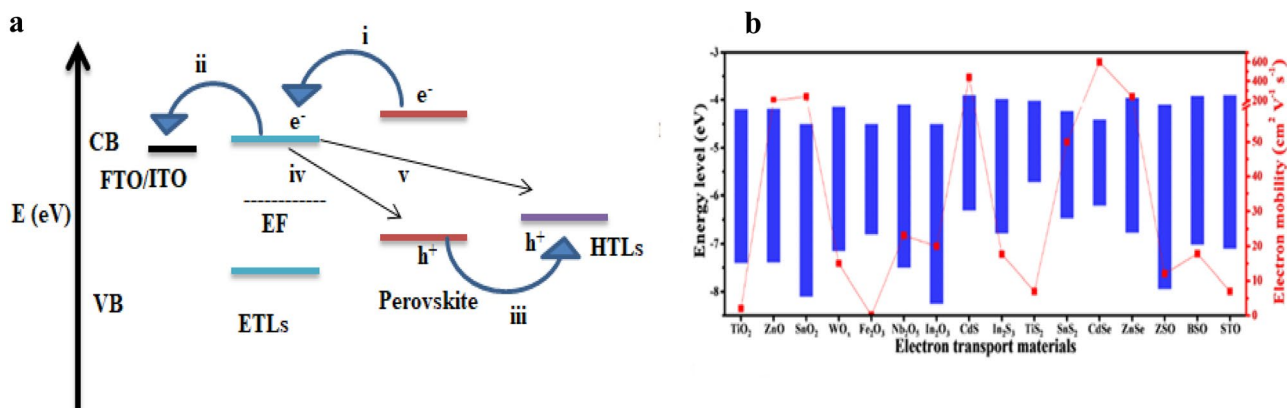


Fig. 5 a Charge transfer mechanism in the ETLs. b Electron mobility and band structure of various electron transport materials [adopted from Refs. 61 and 70]

while the second method involves using bilayer materials for electron transport layers [70, 71].

With doping and undoped electron transport material in PSCs

Doping is one way of improving the conductivity of ETLs and optimizes the energy level matching between ETLs and the perovskite film, leading to increasing the conduction band edge which can efficiently decrease the charge recombination process. Therefore, the electron transport layers have high conductivity, high electron extraction, lower trap-state density, high electron mobility, and transportation process, resulting in enhanced performance of the perovskite solar cell devices, reduced hysteresis, and improved stability [72]. Different research has been developed with different doping materials; for instance, Wang et al. reported the results obtained from poly-vinylpyrrolidone (PVP) doped and undoped SnO₂ as ETLs. The PVP doped SnO₂ thin film exhibits improved electron transport over the undoped one. At the same time, the perovskite grown on PVP-SnO₂ shows more uniform crystalline grains, higher electron mobility, and lower defect density than the control sample grown on the pure SnO₂. The optimized device based on PVP doped SnO₂ exhibited an improved power conversion efficiency of 19.42% compared with the control PSC based on undoped SnO₂. Furthermore, the PVP doped SnO₂-based devices showed reduced hysteresis and better stability without any encapsulation [73]. Recently, Chen et al. proposed an effective approach for producing planar PSCs with Al³⁺ doped SnO₂ ETLs which was prepared by using a low-temperature

solution-processed method. The results revealed that the Al dopant in SnO₂ enhanced the charge transport behavior of planar PSCs and increased the current density of the devices, compared with the undoped SnO₂ ETLs. Moreover, the enhanced electrical property also improved the fill factors and power conversion efficiency of the solar cells. Thus, the optimized cell based on Al-SnO₂ exhibited a higher efficiency of 12.10% than that using SnO₂ (9.02%) as ETLs. The prepared low-temperature solution-processed Al-SnO₂ planar device structure and SEM images are shown in Fig. 6a–c [74]. Similarly, Liu et al. studied the effect of tantalum doping on SnO₂ (Ta-SnO₂) electron transport layer prepared via chemical bath deposition method for perovskite solar cells. The results confirmed that, in contrast to undoped SnO₂, the I-V curve and transmittance spectra showed a significant conductivity improvement of Ta-SnO₂ without declining the light transmittance property. The results further revealed that Ta doping could accelerate the electron transfer and decrease the recombination probability at the SnO₂/perovskite interface, as well as passivated the electron traps, leading to the improvement in the PSC performance. The optimized device showed a power conversion efficiency of 20.80%, with an open-circuit voltage of 1.161 V, a short-circuit current density of 22.79 mA/cm² and a fill factor of 0.786. The device structure and its performance are shown in Fig. 6d–g [75].

Li-doped TiO₂ layer was proposed as a solution to reduce the solar power loss of ETL conductance by Teimouri et al. The doped TiO₂ films have shown significantly improved characteristics by increasing conductivity and providing faster electron transport. A planar PSC device consists of an ETL with 0.3 M Li-doped TiO₂ resulted in a power

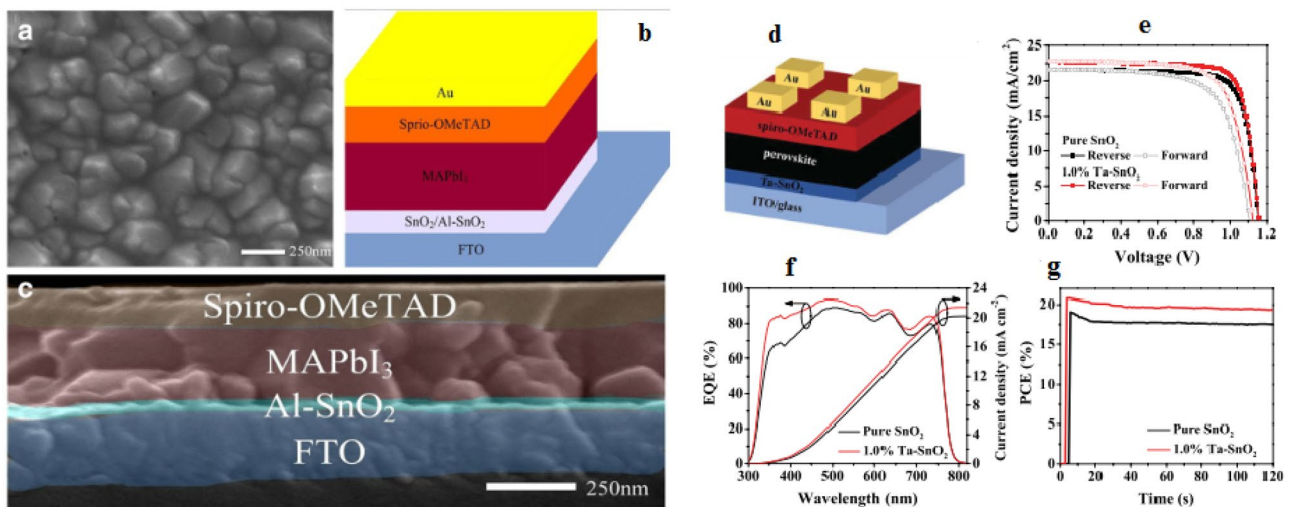


Fig. 6 **a** Top-view SEM image of SnO₂ on FTO. **b** Schematic of the PSCs grown on Al-SnO₂. **c** Cross-sectional SEM image of the planar perovskite solar cell based on Al-SnO₂ [adopted from Ref. 76, open access]. **d** A typical planar PSC structure. **e** J-V curves of **c** PSCs

measured under reverse and forward voltage scanning. **f** EQE of the devices deposited on SnO₂ and Ta-SnO₂ ETLs. **g** Stabilized PCEs for the SnO₂- and Ta-SnO₂-based devices [adopted from Ref. 75]

conversion efficiency of 24.23% which demonstrated 1.97% improvement compared to the one without doping [76]. Yin G and co-workers prepared Nb-doped TiO_2 thin films by simple one-port chemical bath process at low temperature and applied as a high-quality ETL for planar PSCs. Compared with pure TiO_2 , the Nb-doped TiO_2 is more efficient for photogenerated electron injected and extraction showing higher conductivity, higher mobility, and low-state density. A PSC with 1% Nb-doped TiO_2 gives a power conversion efficiency of more than 19% with 1200-h stability in air [77]. Similarly, a better electron extraction and transport, lower trap-state density, and higher conductivity with power conversion efficiency about 17.2% are observed in Sn-doped TiO_2 compared with pristine TiO_2 [78]. For the first time, Mahmood et al. reported highly porous indium-doped ZnO nanofibers by using electro-spinning route as ETLs in PSCs. The high porosity and high crystallinity of the nanofibers give a better infiltration of the absorber and rapid charge transport characteristics due to indium (In) doping. This feature of the material leads to highly efficient and hysteresis-free PSCs with a best power conversion efficiency of 17.18% at optimal thickness. Moreover, the incorporation of polymer polyethyleneimine coated with In-doped ZnO nanofiber ETLs used in PSCs enhanced the power conversion efficiency to 18.69% with free hysteresis. Also, it reduced the work function and the energy barrier, leading to high electron extraction, high conductivity, and good charge transportation [79]. Jeong et al. reported alkali metal carbonates (Li_2CO_3 , Na_2CO_3 , K_2CO_3 , and Cs_2CO_3) doped ZnO nanoparticles as ETLs for the fabrication of planar heterojunction perovskite solar cells. They used low-temperature solution-processed techniques to tune the energy band structure of ZnO ETLs with various alkali metal carbonates. Their results confirmed that the power conversion efficiency of 27% is improved due to the incorporation of alkali carbonates in ETLs.

This is due to the formation of deeper conduction bands in metal carbonates doped ZnO ETLs which leads the electrons can easily transported from the perovskite active layer to the cathode electrode. As alternatives to TiO_2 and n-type metal oxides, electron transport materials consisting of doped ZnO nanoparticles are feasible ETLs for efficient n-i-p planar heterojunction solar cells, and they can be used on flexible substrates via roll-to-roll processing. The schematic diagram of the PSC device and band structure of the metal carbonates doped ZnO is shown in Fig. 7a–c [80]. In general, doing is one of the most important strategies for enhancing intrinsic electronic properties of charge transport layer in perovskite solar cell device. Therefore, increasing the conductivity of the materials ETLs, which is reduced the series resistance contact at the interface of ETLs/ Perovskite absorber layer / electrode also the formation of ohmic contacts to the external electrode, which enhances the fill factor in the perovskite solar cells [81].

Single-layer and bilayer electron transport materials in PSCs

Monolayer (single) charge transport layers have defects and pinholes at the interface; they provide the direct pathways between the perovskite absorber layer and the fluorine-doped tin oxide (FTO)/ITO, which can increase the risk of the recombination between the photogenerated electrons and holes. Besides, they increase the energy loss at the perovskite absorber layer with the interface of both the transparent electrode and ETL [82]. Also, they reduce the blocking effect of electron transport layers, reducing the performance and lifetime of the perovskite solar cell. However, the electron transport bilayer is the most efficient electron transport layer in perovskite solar cells that prevent trapping electrons and the direct contact between perovskite absorber interface and FTO/ITO substrate. Besides, it is important to remove the pinholes and cracks of the surface of charge transport layers. Therefore, the uniform and compact bilayer can effectively avoid charge accumulation to reduce the charge recombination at the interface and back electron transfer from ETLs to perovskite layers also increasing the blocking effect of ETLs then increase open-circuit voltage, short current density, fill factor, and enhanced the performance of the perovskite solar cells [83]. For example, different research has improved the interface between ETLs/perovskite active layer/FTO/ITO substrate by using electron transport bilayer. However, a double-layer TiO_2/WO_3 synthesized by spin coating and atomic layer deposition (ALD) technology can avoid the defect of interfaces between ETLs/perovskite active layers/fluorine-doped tin oxide. This indicates that the minimum loss at the interface of ETLs/perovskite absorber layer/FTO substrate and electron–hole recombination. Therefore, it has higher recombination resistance and lower contact resistance [84]. It has a lower valence band maximum, and the energy level structure can efficiently block the holes than pristine WO_3 and TiO_2 , as shown in Fig. 3. Also fast electron transfer and an efficient electron extraction at interface perovskite absorber layer and bilayer ETLs. In addition, one most important to enhance the performance of perovskite solar cells is controlling the thickness of TiO_2 . The PCE for planar perovskite solar cells exhibited about 20.14% as well as an average PCE of 18.19%, which is better than single TiO_2 or WO_3 of PCE 16.99% or 17.04% reported by You Y and co-workers [84]. In 2018, Yi et al. reported bilayer SnO_2 as an efficient ETL in MAPbI_3 -based perovskite solar cell by a low-temperature solution-processed method. This bilayer of SnO_2 ETLs synthesized using SnO_2 nanoparticle incorporating with a thin layer SnO_2 sol–gel method a uniform and pin-hole free has been formed. Therefore, bilayer SnO_2 ETL devices have lower contact series resistance which implies increasing conductivity of SnO_2 ETLs and charge extraction

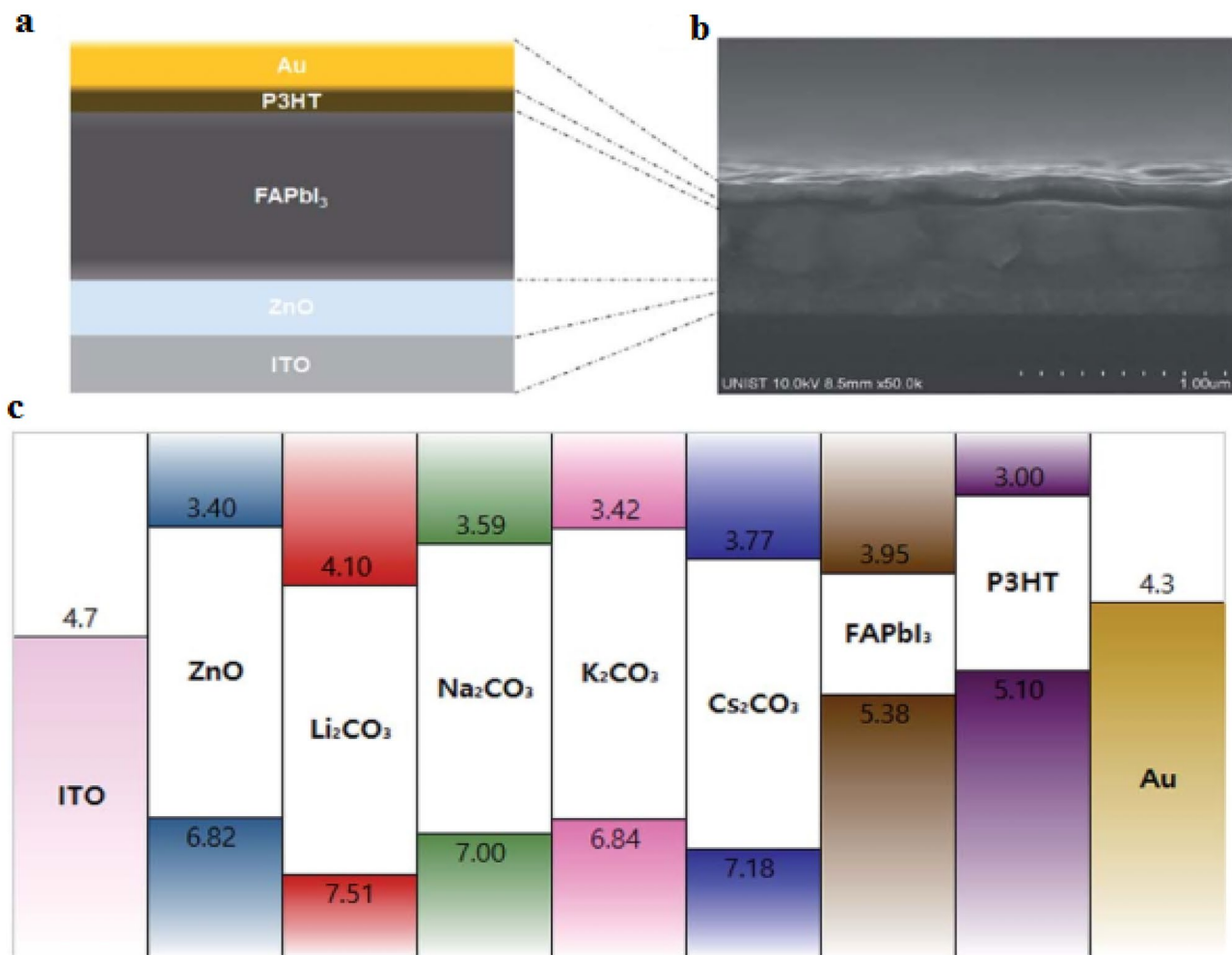


Fig. 7 **a** Schematic diagram of device. **b** SEM cross section images of the conventional planar perovskite solar cell with doped ZnO. **c** Energy band diagram of ZnO doped with various alkali metal carbonate materials [adopted from Ref. 82]

properties at the perovskite/ETL interface. Also, the fewer defects indicate lower recombination of electron–hole at the interface that give higher current density and fill factors and average power conversion efficiency from 12.97 to 16.84% [85]. Martínez-Denegri et al. synthesized SnO₂/TiO₂ nanoparticle at low-temperature and spin-coating method as ETL bilayers. They demonstrated that a few tens of nanometers thick bilayer can perform as a robust. Aside from boosting the average efficiency of planar opaque devices, the proposed method allowed them to preserve the main photovoltaic characteristics when thinner active layers, usually exhibiting a noncontinuous morphology, were integrated for semitransparent cells. The bilayers of ETL power conversion efficiency exhibited from 14.9 to 15.2% and short-circuit photocurrent and fill factor values which are higher than that of monolayer [86]. Lu H and co-workers successfully designed a novel TiO₂ bilayer with type II band alignment at different Fermi energy levels by combing atomic layer deposition and spin-coating technique. Their

results verified that the TiO₂ bilayer-based perovskite solar cells were highly efficient in carrier extraction, recombination suppression, and defect passivation, and thus demonstrate champion efficiencies up to 16.5%, presenting almost 50% enhancement compared to the TiO₂ single-layer-based counterparts [87]. F-doped SnO₂ nanocrystals using facile low-temperature solution-processed method as bilayer ETL planar heterojunction perovskite solar cells was reported by Gong et al. They found that a gradual substitution of F⁻ into the SnO₂ ETL can effectively reduce the band offset and result in a substantial increase in device open-circuit voltage. As a result, a power conversion efficiency of 20.2% was achieved for planar heterojunction PSCs using F-doped SnO₂ as bilayer ETL. Furthermore, reduced the charge accumulation of at the interface between ETLs and perovskite active layer leads reducing energy loss due to high charge extraction and transport at interface [88]. Li et al. introduced a low-temperature solution method to deposit a TiO₂/SnO₂ bilayer for an efficient ETL. The results demonstrated that

the $\text{TiO}_2/\text{SnO}_2$ ETL has an enhanced charge extraction ability and a suppressed carrier recombination at the ETL/perovskite interface, which gives a better photogenerated carrier separation and transport for $\text{TiO}_2/\text{SnO}_2$ bilayer ETL. As a result, PSCs with $\text{TiO}_2/\text{SnO}_2$ bilayer ETLs present higher photovoltaic performance of the baseline cells compared with their TiO_2 and SnO_2 single-layer ETL counterparts. The optimized PSC device has a power conversion efficiency of 19.11% with an open-circuit voltage of 1.15 V, a short-circuit current density of 22.77 mA cm^{-2} , and a fill factor of 72.38% shown in Fig. 8a [85]. Due to the suitable band alignment Fig. 8b of the $\text{TiO}_2/\text{SnO}_2$ ETL in the device, a high open-circuit voltage of 1.18 V is achieved. The obtained J-V values, band gap alignment, and PL spectra are depicted in Fig. 8a–d [89]. In another work, Xu et al. prepared TiO_2/ZnO bilayer by employing a sol–gel method as ETLs for perovskite solar cells. These bilayers improved the interfacial layer by avoiding the direct contact between the FTO substrate and perovskite active layer. Moreover, this bilayer, together with perovskite absorber, forms a type II energy band structure benefiting high charge extraction and transport leading to lower electron–hole recombination in the cells and improved final power conversion efficiency

from 13.2 to 17.2% [83]. Similarly, Kumari et al. synthesized TiO_2/ZnO by spray pyrolysis technique method as ETLs for perovskite solar cells. This bilayer helps in high electron extraction and low interfacial recombination due to high charge collection and transportation, therefore lower charge accumulation at the interface between ETLs and perovskite active layer.

In addition by using 4-tert-butylpyridine (TBP) increase in the contact angle of prepared films reduces the of degradation of perovskite film into PbI_2 under moisture. This enhanced the stability of perovskite solar cells. Moreover, controlling the effect of precursor concentration, thickness, substrate temperature, and solution flow rate is important to determine optimization condition of TiO_2 film. The highest power conversion efficiency of about 7.39% was found for the device with TBP [90]. For the first time, Wang et al. reported the highest open-circuit voltage around 1.15 V for ZnO/SnO_2 double layer as ETLs with a power conversion efficiency 18% [91]. The benefits of low-temperature processed fullerene/ SnO_2 bilayers as ETLs for efficient planar perovskite solar cells were investigated by Chen Y and co-worker. The results show that the existence of PC_{60}BM could enhance the crystalline quality and grain boundary

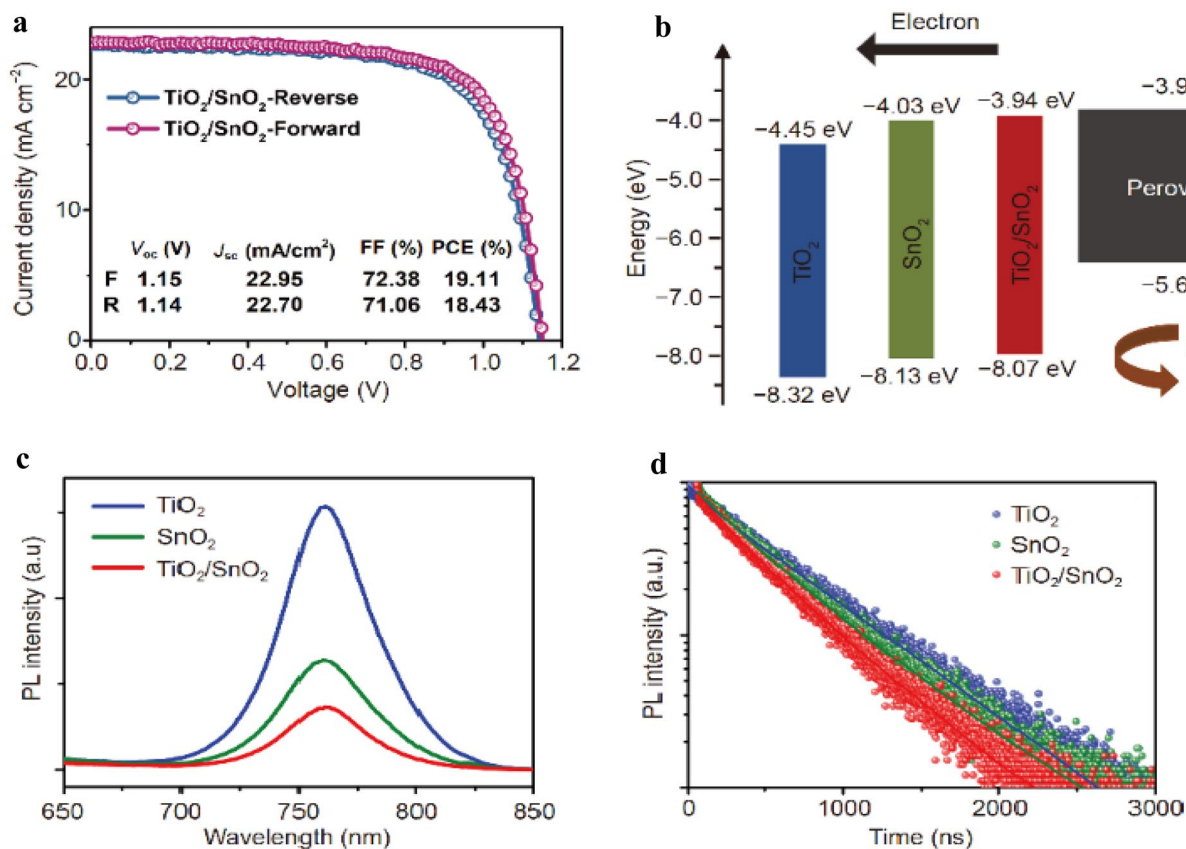


Fig. 8 **a** The J-V curves of the PSC based on $\text{TiO}_2/\text{SnO}_2$ bilayer ETL. **b** Band alignment for different ETLs: TiO_2 , SnO_2 , and $\text{TiO}_2/\text{SnO}_2$. **c** PL spectra and **d** time-resolved PL curves of perovskite film deposited on different ETLs: TiO_2 , SnO_2 , and $\text{TiO}_2/\text{SnO}_2$ [adopted from Ref. 91]

integration in perovskite films. The J-V analysis and other experimental results revealed that both the light harvesting of perovskite films and carrier extraction from perovskite films to PC₆₀BM/SnO₂ bilayer have been enhanced. The device performance shows a higher average PCE 15.03% and also improved short-circuit current density about 21.05 mA·cm⁻² [92]. Corresponding, different researcher has been enhanced the performance of the perovskite solar cells were used a bilayer as the electron transport layer in perovskite film. Hence improved the interface between electron transport layer/perovskite active layer / FTO substrate and prevent direct contact of them also improved the charge extraction and transportation indicate reduce charge accumulation, energy loss and trap-state density also suppressed electron hole recombination such as ZnO-PCBM [93], SnO₂/ZnO [94], PCBM/CeO_x [95], ZnO/AZO [96], TiO₂/SnO₂ [97].

Interface engineering

Interface engineering for conventional PSCs

SAMs Self-assembled monolayers (SAMs) were utilized to change the dielectric and drain electrode surfaces of electron-selective transfer layers made of metal oxide. Thermodynamically, self-assembly of molecules on the surface is a process in which molecules interact with one another to produce structured structures. Surface passivation dielectrics such as SiO₂ or Al₂O₃ are the most often used [98]. SAMs improve the shape and crystal quality of the perovskite layer by improving crystallinity, increasing grain size, and lowering the degree of defects at the surface. Furthermore, fine-tuning the polarity of molecules to manage the interfacial dipole moment in relation to the normal surface indicates a change in the work function [99]. As a result, changing the surface morphology of perovskite solar cells reduces charge carrier traps and energy loss at the interface, resulting in improved charge extraction and transportation from the active layer of the perovskite. As a result, reducing charge accumulation at the interface causes charge recombination to be suppressed and hysteresis to be reduced [100]. This is modified by the surface energy of dielectric materials. The modification of electron transport layer interface and perovskite active layer with functional SAMs has been causing improvement in electrical parameters which can contribute to increasing the efficiency of perovskite solar cell device [101, 102]. The combination of SAMs with metal oxide such as TiO₂, ZnO, and SnO₂ further improves the interface properties of perovskite solar cells. Modifying the surfaces of noninverted (SnO₂) and inverted (NiO_x) films with ethylphosphonic acid (EPA) and 4-bromobenzoic acid (BBA) SAMs does not necessarily lead to enhanced

efficiency, but the stability is greatly enhanced and hysteresis of the films are reduced [103]. Recently, a fullerene derivative pyrrolidinofullerene C60-substituted phenol (NPC60-OH) was introduced to modify the surface SnO₂ ETLs, which reduced the energy band gap between ETL and the perovskite film due to the suitable work function of SnO₂/NPC₆₀-OH. Therefore, high conductivity of ETL leads to high charge mobility and transportation, hence suppresses charge recombination and lower trap-state density at interface. However, the electrical parameter of Voc, J_{sc}, and FF are enhanced and the power conversion efficiency has reached 21.39% but lower hysteresis and more stable device than pure SnO₂ [104]. Modify the surface of ZnO ETL with methoxybenzoic acid derivatives (3,4,5-trimethoxybenzoic acid) (TMBA) which made a larger work function shift of ZnO ETL and high charge extraction and transfer due to improved conductivity. Moreover, reduced electron-hole recombination, lower trap-state density, and hysteresis, which is higher open-circuit voltage than the power conversion efficiency has been found from 1.44 to 13.75% [105]. A self-assembled monolayer of γ -mercaptopropyltrimethoxysilane (γ -MPTS) was used to modify the interface between the meso-TiO₂ surface ETLs and the perovskite layer which leads to minimized trap-state density and improved the carrier transport performance. Also, the electron-hole recombination and the power conversion efficiencies were achieved from 14.36 to 16.50% which less hysteresis, hence better performed than unmodified TiO₂ [106]. Modified the surface of WO_x layer with SAM layer used a low-temperature process, the J_{sc}, V_{oc}, FF, and PCE were improved. Therefore, power conversion efficiency was reached to 14.9% without any hysteresis [107].

Window layer passivation Improving the interface between ETLs and the perovskite absorber layer is an effective method for suppressing the charge recombination. Therefore, using a wide layer controlling the charge recombination at the surface of TiO₂, SnO₂, ZnO, and WO₃. The interface between the TiO₂ layer and the perovskite layer was modified by an ultrathin MgO nanolayer. This MgO-coated TiO₂ film suppresses charge recombination at the TiO₂/CH₃NH₃PbI₃ surface, which leads to the improvement in both V_{oc} and FF; therefore, an increase of PCE from 11.4 to 12.7% was demonstrated [108]. An ultrathin Zn₂SnO₄ (ZTO) layer was coated onto ZnO nanocone via a solution-processed method to modify the interface between the ZnO layer and the perovskite layer. This ZTO-coated ZnO film could retard the charge recombination at ZnO/perovskite active layer surface. This combination showed an improvement in all PV parameters with power conversion efficiency about 18.3% [109]. The surface modification of ZnO covered the ultrathin Nb₂O₅ passivation layer

synthesized by the sol–gel method, which could reduce ZnO surface defects and also improved the morphology of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite film. The ultrathin Nb_2O_5 passivation layer effectively prevents direct contact between the ZnO and perovskite and prevents the decomposition of the perovskite light absorber coated over ZnO.

Therefore, an efficient charge transport layer leads suppress charge recombination and improved power conversion efficiency to 14.57% [110]. Fullerene derivative pyrrolidinofullerene C_{60} -substituted phenol (NPC₆₀-OH) modified surface of SnO_2 ETLs reduce the charge recombination and trap-state density indications enhance the electron mobility and transportation of perovskite solar cells. Furthermore, The NPC₆₀-OH-based devices showed a reduced energy band gap between ETL and the perovskite film due to the suitable WF of $\text{SnO}_2/\text{NPC}_{60}\text{-OH}$, which contributed to the high open-circuit voltage and improved power conversion efficiency [104].

Stability and performance of perovskite solar cells

Perovskite solar cells' long-term stability is a significant consideration for commercial use. As a result, a variety of factors affecting perovskite solar cell stability, such as moisture, oxygen, temperature, and UV radiation stability, must be carefully evaluated [111, 114]. Different researchers have focused on improving the stability of PSCs by introducing moisture, oxygen, UV light, and thermal-resistant layers. For example, Wang et al. reported that polyethylene glycol (PEG) into the methylammonium lead trihalide (MAPbI_3) precursor solution, with $\text{TiO}_2\text{-ZrO}_2$ mesoporous scaffold as ETLs in PSCs with carbon electrode and the hole-conductor-free. The hygroscopic PEG protects the perovskite film from moisture which leads exhibit superior stability and enhanced the power conversion efficiency of 11.62% [100]. Cesium iodide doped in methylammonium lead iodide perovskite ($\text{Cs}_x\text{MA}_{1-x}\text{PbI}_3$) as light absorber layer with carbon counter electrode and hole-conductors-free perovskite solar cell were fabricated under a high humidity air environment. The results revealed that the presence of cesium and carbon improved the moisture-resistant of the perovskite solar cell devices with high stability and enhanced power conversion efficiency [112]. Modifying the interface between mesoporous TiO_2 /perovskite layer were used both aminocaproic acid [$\text{H}_2\text{NCH}_2(\text{CH}_2)_4\text{COOH}$] and caproic acid [$\text{CH}_3(\text{CH}_2)_4\text{COOH}$], leading to significant enhancement in both the efficiency and stability of PSCs. This modified mesoporous TiO_2 /perovskite layer of power conversion efficiency was found 18.2% and improving the stability of PSCs under $50 \pm 5\%$ relative humidity in the air [113].

Conclusion and future perspective

Charge transport layers in perovskite solar cells may serve as n-type to couple the half in a p–n junction, reduce surface recombination at the interface, conduct the current to the metal electrode, and allow the incoming light to pass the maximum portion through and reach the absorber layer. Therefore, in this review, we have presented efforts that have been made to improve the PCE using a single layer and bilayer of ETL, the interface between the ETL, and the perovskite absorber layer. The effects of doping on the properties of ETL in perovskite solar cells were thoroughly discussed. Various metal oxides such as TiO_2 , ZnO, SnO_2 , WO_x , and fullerene and their derivatives as ETLs have been researched and applied to perovskite solar cells. The charge collection efficiency of single ETL of the TiO_2 -based ETL has been improved by using bilayers such as $\text{TiO}_2/\text{SnO}_2$, TiO_2/ZnO , TiO_2/WO_3 , and appropriate substitution of cation doping such as Nb, Sn, and Li. The improved charge collection performance using bilayer and doped ETL may arise due to the reduction of charge carrier recombination at the surface, enhancing the current conduction ability of the layers. It also noted that the interface between the charge transport layers and perovskite active layer modifications with functional self-assembled monolayers (SAMs) is important for enhancing charge extraction and transportation. Besides, suppressing charge recombination indicates enhanced performance and stability in perovskite solar cell devices. Therefore, to harness the widest portion of visible light-generated charge carriers using perovskite solar cells needs careful design of the ETL and interfaces. It possibly boosts the efficiency, and a hysteresis-free perovskite solar cell device was constructed for commercial application. Therefore, bilayers ETL will improve the PCE of perovskite solar cells by improving the current conduction through them to the metal electrode, enhancing the amount of light passing through to the photon active layer, and reducing charge carrier recombination at the surface and interface.

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