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N-type metal-oxide electron transport layer for mesoscopic perovskite solar cells

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ABSTRACT To meet the challenge of continuously increasing global energy demands, organic-inorganic halide based perovskite solar cells (PSCs) have garnered great attention from the photovoltaic research community for their low cost and high efficiency. The efficiency of perovskite-based mesoscopic solar cells increases rapidly, from 3.8% in 2009 to 22.1% in 2016. N-type metal-oxide electron transport layer, as one of the important components in mesoscopic PSCs (MPSCs), acts as not only a scaffold layer for the growth of perovskite crystals, but also a layer to supply transfer pathways for electrons injected from perovskites. In this review, we discussed recent published reports of MPSCs with the focus on n-type metal-oxide electron transport layer in MPSCs. The scaffold materials, scaffold nanostructure, and scaffold/perovskite interface engineering are considered, and the effects of these modifications of scaffolds on the performance of MPSCs are summarized in this review.

Keywords: n-type electron transport materials, mesoscopic, perovskite solar cells, electron transport, scaffold nanostructure

INTRODUCTION

In terms of the energy issues faced by global sustainable economy development, economically viable renewable energy sources are very essential, in which solar energy is one of the best candidates to satisfy the future global need for renewable energy sources [1]. A great deal of attention has been paid on solar cells, which possess direct conversion of solar energy to electric energy. Dye-sensitized solar cells (DSSCs), known as the Grätzel cell, were first fabricated by Grätzel's group in 1991 [2] and perovskite solar cells (PSCs) were evolved from DSSC by using perovskite hybrid as the light harvester [3]. The first use of perovskite in solar cells did not show a high efficiency. In 2009, Kojima *et al.* [3]

employed $\text{CH}_3\text{NH}_3\text{PbI}_3$ and the analogue $\text{CH}_3\text{NH}_3\text{PbBr}_3$ as sensitizers in liquid-electrolyte-based DSSC, yielding a low power conversion efficiency (PCE) of only 3.81%. Due to the solvation of perovskites in acetonitrile, the photocurrent decayed under continuous irradiation. A key advance was made in 2012 by replacing the liquid electrolyte with a solid hole transporting material (HTM), leading to a high PCE of 9.7% and enhanced cell stability [4]. Then, the certificated PCE was boosted to 22.1% in 2016 [5], as tremendous efforts have been devoted to the research of PSCs, including the primary mechanism, various materials fabrication methods and architecture design.

The general chemical formula of perovskite compounds is ABX_3 , where, for typical, X is a halogen ion (I^- , Br^- , Cl^- or their alloys) that bonds to the A and B cations, A is typically CH_3NH_3^+ (MA^+), $\text{NH}_2\text{CHNH}_3^+$ (FA^+), Cs^+ or their alloys, and B is typically Pb^{2+} , Sn^{2+} or their alloys. They have a suitable direct band gap and an intense absorption over the entire visible region, showing superior photovoltaic properties. The PSCs structure geometry is shown in Fig. 1, which is typically composed of transparent electrode, counter electrode, light harvesting perovskite layer, hole transport layer (HTL) and electron transport layer (ETL). The perovskite layer is either adsorbed on the scaffold materials or prepared as a compact film, and these two typical structures exist in mesoscopic PSC (MPSC) and planar PSC. Two typical types of MPSC (A and B), corresponding to the two types of planar PSC (C and D), are shown in Fig. 1. Using perovskite with both high mobility of electron and holes, PSC without HTL or ETL were also fabricated. The HTL-free PSC shows a particular good industrialization prospect due to the removal of expensive

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Figure 1 Perovskite crystal structure (center) and cell structures: A and B, MPSC; C and D, planar PSC.

HTL materials [6–9]. Han's group made HTL-free MPSC with excellent stability and an efficiency of 12.8% in 2013 [7]. Based on carbon electrode, the structure has triple printable mesoscopic layers, showing a great potential in the large-scale application. Fig. 2 illustrates the cross section of the triple-layer perovskite-based fully printable mesoscopic solar cell.

Compared to the planar PSC, MPSC with a mesoporous scaffold provides a simple and straightforward way to achieve controllable crystallization and good surface contact [10]. If the scaffold participates in the photoelectric

Figure 2 Schematic drawing showing the cross section of the triple-layer perovskite-based fully printable mesoscopic solar cell. The mesoporous layers of TiO_2 and ZrO_2 have a thickness of ~ 1 and $2 \mu\text{m}$, respectively, and are deposited on a FTO-covered glass sheet shown in blue and gray. They are infiltrated with perovskite by drop-casting from solution. Reprinted with the permission from Ref. [7], Copyright 2014, the American Association for the Advancement of Science (AAAS).

conversion process, it can be considered an active component in the perovskite solar cell, defined as “active scaffolds”, while if the scaffold does not participate actively in the charge transport and only act purely as a supporting scaffold for perovskites, it is considered as a “passive scaffold”. The typical example for the active and passive scaffold is TiO_2 and Al_2O_3 , respectively. Fig. 3 demonstrates the charge transfer and charge transport in TiO_2 and Al_2O_3 -based PSCs with the representation of the energy landscape [11].

Most of the active scaffolds are based on n-type metal-oxide semiconductors and they play an important role in achieving a high efficiency of MPSC, so numerous studies were carried out. In this review, the recent progress of active n-type metal-oxide scaffold for applications in MPSCs is comprehensively summarized. Emphasis is placed on the three aspects of the n-type ETL: materials, nanostructure and interface engineering. Firstly, the materials used as the ETL were summarized, including traditional binary oxide materials, alternative ternary oxides materials and modified materials; secondly, the morphology control and modification of the nanostructures were described; finally, the recent progress of the materials and technologies associated with interfacial engineering were discussed.

MATERIALS

TiO_2 has three crystalline phases in nature, including rutile, anatase, and brookite. The anatase phase has the highest active performance in many applications compared to the other two phases [12]. Moreover, TiO_2 is cheap, nontoxic, chemically inert and absorbs only below 388 nm making it invisible to most of the solar spectrum, thus reducing the recombination rate of photo injected electrons [13]. These enables the anatase TiO_2 as the most common materials used for ETL in MPSC. Until now, most of the high efficient PSCs are obtained by using anatase TiO_2 nanocrystals as ETL in the published papers [14–16].

Lee *et al.* [17] reported that the photo-excited electrons generated by perovskite are in part injected to TiO_2 and the extent of electron injection can be influenced by the crystal phase of TiO_2 . Their results show that the rutile TiO_2 -based MPSC had a higher J_{SC} and lower V_{OC} in comparison with anatase TiO_2 -based MPSC, as slower electron transport and longer electron lifetime were observed for the rutile-based PSC than that for the anatase-based one. Kogo *et al.* [18] fabricated a mesoporous brookite TiO_2 by a sinter-free solution process and applied it in MPSC. The obtained cell showed a photovoltaic performance with a greater fill factor and 100 mV-higher V_{OC} than the cell made with an anatase

Figure 3 Schematic illustrating the charge transfer and charge transport in a perovskite-sensitized TiO_2 solar cell (left) and a noninjecting Al_2O_3 -based solar cell (right); a representation of the energy landscape is shown below, with electrons shown as solid circles and holes as open circles. Reprinted with permission from Ref. [11], Copyright 2012, AAAS.

TiO_2 mesostructure prepared by high temperature sintering. This is because the mesoporous brookite TiO_2 has a bit lower electron mobility combined with a slightly more negative conduction band (CB) edge potential than that of anatase TiO_2 , which may decrease recombination without causing voltage loss.

As shown in Fig. 4, some binary and ternary oxides materials with suitable band gap are explored as a replacement of anatase TiO_2 . The performance of the PSC fabricated with these ETL materials are summarized in Table 1. Among them, ZnO ($100\text{--}150\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) [19], SnO_2 ($240\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) [20], Zn_2SnO_4 ($10\text{--}15\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) [21], BaSnO_3 ($\sim 70\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) [22] and SrTiO_3 ($5\text{--}8\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) [23] have higher electron mobilities than anatase TiO_2 ($0.1\text{--}4\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) at room temperature. A high electron mobility of ETL materials allows a fast electron transport and an efficient charge collection, which may contribute to a better solar cell performance.

BaSnO_3 and SrTiO_3 are transparent semiconducting perovskite oxides with the same perovskite structure as MAPbI_3 . Zhu *et al.* [24] and Bera *et al.* [25] explored BaSnO_3 and SrTiO_3 as the replacement of TiO_2 in MPSCs, respectively. Both of them found that the alternative

scaffold affected the crystal growth and morphology of perovskite. The cell performance of BaSnO_3 - and SrTiO_3 -based MPSCs performs as well as the TiO_2 one and even better. This is because, besides the faster electron transport BaSnO_3 and SrTiO_3 have a better contact with perovskite, which makes the crystals grow more unity and the scaffold have a better surface coverage, resulting in a high shunt resistance and improved performance compared with the conventional mesoporous TiO_2 in the control device. Recently, Bera *et al.* [26] also reported that the mesoporous ternary oxide Zn_2SnO_4 could significantly promote the crystallization of hybrid perovskite layers and serve as an efficient electron transporting material in perovskite solar cells, although the Zn_2SnO_4 was firstly used as ETL in MPSC by Oh *et al.* [27]. Both of them noticed that the Zn_2SnO_4 -based PSC exhibited much faster electron transport and superior charge collection capability than TiO_2 -based PSC under similar condition. In Bera's work, the Zn_2SnO_4 -based $\text{MAPbI}_{3-x}\text{Cl}_x$ PSC exhibited a PCE of 13.34%, which is even higher than that achieved with the commonly used TiO_2 in the similar experimental conditions (9.1%). Most importantly, the solar cells show negligible electrical hysteresis and exceptionally high sta-

Figure 4 Schematic diagram illustrating the energy levels of CB and valence band (VB) of n-type metal-oxide electron transport materials according to references.

Table 1 A summary of the published representative results of MPSCs' performance parameters with different scaffold materials

Scaffold material	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	Ref.
Anatase TiO ₂ ^{a)}	23.5	1.06	77	20.1	[14]
Rutile TiO ₂	20.0	1.02	71	14.5	[17]
Brookite TiO ₂	20.6	1.00	70	14.3	[18]
BaSnO ₃	16.8	1.03	71	12.3	[24]
SrTiO ₃	14.8	0.93	55	7.6	[25]
Zn ₂ SnO ₄ ^{b)}	19.6	0.94	73	13.3	[26]
SnO ₂	10.9	0.55	63	3.8	[28]
WO ₃	6.5	0.78	75	3.8	[29]
ZnO	12.7	0.68	58	5.0	[31]
N doped ZnO	17.5	0.96	63	11.7	[32]
Nb doped TiO ₂	18.7	0.99	72	13.4	[34]
Sn doped TiO ₂	14.9	0.74	52	6.3	[35]
Mg doped TiO ₂ ^{c)}	10.4	0.80	50	4.2	[36]
Zn doped TiO ₂	20.1	1.02	76	15.6	[37]
Zr doped TiO ₂	20.3	1.02	77	15.7	[37]
Mo doped TiO ₂	20.0	1.01	76	15.4	[37]
Y doped TiO ₂	18.1	0.94	66	11.2	[38]
Graphene & SrTiO ₃ composites	18.1	1.00	58	10.5	[40]
TiO ₂ & ITO composites	16.4	0.74	63	7.5	[41]

The cell configuration is fluorine doped tin oxide (FTO)/compact-TiO₂ (or ZnO)/scaffold/MAPbI₃/spiro-OMeTAD/Au (or Ag) without specification.

a) FTO/compact-TiO₂/scaffold/(FAPbI₃)_{0.85}(MAPbBr₃)_{0.15}/polytriarylamine/Au; b) FTO/compact-Zn₂SnO₄/scaffold/MAPbI_{3-x}Cl_x/spiro-OMeTAD/Au;

c) FTO/compact-ZnO/scaffold/MAPbI₃/P3HT/Au.

bility without encapsulation for over one month, demonstrating that Zn₂SnO₄ could be a suitable candidate as ETL to replace TiO₂.

Zhu *et al.* [28] reported the first synthesis of mesoporous SnO₂ single crystals and its application in PSC. A relatively low efficiency was obtained due to the strong charge recombination at the SnO₂/perovskite interface, although the charge mobility of SnO₂ is almost two orders of magnitude higher than that of TiO₂. WO₃ with different

nanostructures were used as ETL according to the report by Mahmood *et al.* [29]. The nanostructure morphology strongly influences the photocurrent and efficiency in MPSC. Among them, the PSC based on WO₃ nanosheet arrays yield significantly enhanced photovoltaic performance as compared to nanoparticles and nanorod arrays due to good perovskite absorber infiltration in the porous scaffold and more rapid carrier transport. However, the SnO₂ and WO₃-based PSCs show a relatively low efficiency

which is incomparable to the TiO_2 -based one due to the higher recombination rate.

ZnO is another widely used material in the area of photovoltaics. It shares many similar characteristics as anatase TiO_2 but has several orders of magnitude higher conductivity than anatase TiO_2 [30]. The first example of a ZnO-based MPSC was reported by Bi *et al.* in 2013 [31], where the solar cell showed a good long term stability with an efficiency of 5.0%. However, compared to the TiO_2 -based solar cells, the ZnO-based one shows a lower performance due to a much higher recombination rate in the surface and interfacial defects within the oxide and between the oxide and the perovskite absorber. And one effective way to reduce the defects and improve the electron transport property is doping. Mahmood *et al.* [32] used N doped ZnO nanorods as ETL and a significant efficiency improvement was reported. Increases in J_{SC} and PCE resulting from N doping were attributed to the increase in the electron density caused by the doping. V_{OC} increase is due to the reduced recombination losses within the nanorods and an increase in their Fermi energy levels, owing to the increase in the charge-carrier density, which broadens the direct optical bandgap and lowers the barrier of electron transfer.

The band gap modification effect of doping is often reported in TiO_2 ETL as well. Nb doping was reported in both TiO_2 nanorods and nanoparticles. Yang *et al.* [33] fabricated Nb doped rutile TiO_2 nanorods and the PSC with Nb-doped rutile nanorods had significantly improved performance, because the positively shifted flat band of Nb doped TiO_2 favored electron injection. Nb doping can also improve the electron transport and collection by providing a high conductive path and better interface contact. Kim *et al.* [34] fabricated Nb doped TiO_2 nanoparticles and discussed the effect of doping amount in the shift of band gap. Light doping increases the band gap slightly but heavy doping decreases it obviously. The light Nb doped TiO_2 -based PSCs exhibit higher efficiency (13.4%) than the PSC based on undoped TiO_2 (12.2%) and the PSC utilizing heavily doped TiO_2 nanoparticles (8.8%), which is attributed to fast electron injection/transport and preserved electron lifetime.

Besides Nb, Sn and Mg elements are successfully doped in TiO_2 rutile nanorods showing an improved efficiency in the doped materials based MPSC than the undoped ones due to the shift of band gap and lowered recombination rate [35,36]. Wang *et al.* [37] invented a general, facile and quantitative rout to prepare a series of doped TiO_2 materials. The doping elements vary from Zn, Y, and Zr to Mo. Taking Y as an example, yttrium acetylacetonate hydrate

was precisely added into titanium acetylacetonate hydrate, and Y doped TiO_2 could be obtained after calcination. After doping, the TiO_2 ETL in PSC has an enhanced device performance, particularly pertaining to J_{SC} and fill factor (FF) due to a better carrier extraction and the band gap shift.

Besides the variation of band gap, doping can modify the surface states and has a further influence on the materials that adsorbed on its surface. Grätzel's group fabricated Y doped TiO_2 and the MPSC made from the doped TiO_2 ETL showed an enhanced performance [38]. Yttrium is poorly soluble in TiO_2 and segregation of Y_2O_3 at the surface facilitates an increased material loading and further affects the morphology of light harvester. A PCE of 11.2% was measured with a 15% improvement in the J_{SC} compared with pure TiO_2 , because of the upward shift of the CB, depressed recombination rate and the effects of surface modification that further affects the loading and morphology of perovskite.

To improve the charge collecting efficiency, the materials with super electron mobility are introduced into TiO_2 films to form nanocomposite film. Graphene has a fast electron transfer and is successfully used in photovoltaic devices [39,40]. In the work of Wang *et al.*, they used graphene/ TiO_2 nanocomposites as an effective ETL [39]. Due to the high transparency and electron mobility of the graphene, the device based on graphene/ TiO_2 nanocomposites exhibits a PCE up to 15.6% for low-temperature PSC. One dimensional (1D) materials have an acknowledged faster electron transport although accompanied with a relatively lower surface area than three dimensional (3D) materials. Combining the two kinds of materials together may improve the electron transport efficiency and the loading of light harvester in MPSC. Han *et al.* [41] prepared TiO_2 /indium tin oxides (ITO) nanocomposite antenna for ETL in MPSC, where the ITO has a 1D nanowire structure and a native high conductivity and TiO_2 forms nanoparticles with a relatively high surface area. The superior charge collection properties of the TiO_2 nanoparticle and ITO nanowire composite materials are responsible for the boosted current densities of the TiO_2 /ITO nanocomposite MPSC than that of TiO_2 nanoparticles.

NANOSTRUCTURE

The specific surface area and surface-to-volume ratio increase remarkably as the size of materials decreases. Additionally, the movement of electrons and holes in semiconductor nanomaterials and the transport properties related

to photons are largely affected by the size and geometry of the materials [42]. So, considerable effort has been devoted to the fabrication of nanosized TiO_2 and TiO_2 with nanostructures [43].

TiO_2 nanocrystal is the common materials used in ETL of PSCs. The size of nanoparticle plays an important role in the performance of PSC. Generally, the nanoparticles with a smaller size have a higher surface area than that with the bigger ones, while the pores formed in films made from tiny crystals are smaller than that from the big ones. Surface area and pore size are two main factors that affect the loading of perovskite in MPSCs, so an appropriate size of nanoparticle should be considered. Han's group studied the TiO_2 with different sizes in the HTL-free fully printable MPSCs [44]. The results show that the size of TiO_2 particles not only affects the infiltration of the precursor and the contact between the perovskite crystal and TiO_2 , but also significantly affects the charge transfer kinetics at the perovskite/ TiO_2 interface. With the TiO_2 nanoparticles with an optimized diameter of 25 nm, the carbon counter electrode based MPSC exhibits the best PCE of 13.41%.

Compared to TiO_2 crystallites, TiO_2 with 1D or 2D nanostructure, such as rods, belts and tubes, is considered to have some advantages in electronic and photonic devices [45–47]. Rutile nanorods with the length controlled by the hydrothermal reaction time were fabricated in Park's group [48]. The TiO_2 was applied in MPSC and the photovoltaic performance was significantly dependent on the length of the nanorods, as the amount of adsorbed perovskite and pore filling fraction are closely related to the rods length. The V_{OC} and PCE decrease with the increase of nanorod length. The optimized cell shows a J_{SC} of 15.6 mA cm^{-2} , V_{OC} of 955 mV, and FF of 0.63, yielding a PCE of 9.4%.

Zhong *et al.* [49] prepared single-crystalline rutile TiO_2 nanocones with adjustable length. Applied the materials into MPSC, the cell yields 11.9% PCE, which is superior to the control cell (10% for TiO_2 nanorods and 11% for ZnO nanorods, respectively). This is because the electron transfer from perovskite to the TiO_2 nanocones is significantly faster than to the TiO_2 nanorods, which is an important factor to suppress charge recombination and improve device performance.

Jiang *et al.* [50] fabricated length-controllable rutile nanowire arrays with fully accessible and wide-open inter-wire voids. These TiO_2 nanowires were used as photoanodes for PSCs. Optimized cells with 900 nm nanowires as photoanodes exhibited a J_{SC} of 22 mA cm^{-2} and an efficiency of 11.7%, which is the highest efficiency of the reported TiO_2 nanowire-based PSCs. However, so

far the highest efficiency reported on 1D TiO_2 nanostructure-based PSC was obtained by Nazeeruddin's group [51]. They prepared submicrometer highly ordered and transparent TiO_2 nanotube array films and the obtained MPSC yielded a J_{SC} of 22.6 mA cm^{-2} and PCE of 14.8%. Despite having relatively low loading of perovskite, more efficient charge collection/extraction on nanotube-based electrodes contributes to the improved photovoltaic parameters. Moreover, the unsealed TiO_2 nanotube-based devices are remarkably stable in light soaking test which could be attributed to the self-sealing property of the nanotubes.

To overcome the issue of low loading of perovskite on 1D materials, 3D hyperbranched anatase TiO_2 nanorod-nanofiber arrays were adopted by Mahmood *et al.* [52]. The hyperbranched nanorod-nanofiber arrays exhibited a large surface area along with the rapid charge transport and reduced recombination, leading to a remarkable enhancement of photovoltaic efficiency. The obtained PSC using a submicron layer of the hyperbranched arrays yields a high PCE of 15.20%.

Another widely used 1D structure is ZnO nanorod. Park's group did much work on the control of ZnO nanorods morphology and discussed its effects on the performance of nanorod-based MPSC [53,54]. They fabricated ZnO nanorods with different diameters and lengths, also discussed the effects of seed layer on the growth of ZnO nanorods. These materials with different morphologies were used as ETL in PSC, showing various cell performances. By controlling the precursor concentration and growth time, the length of ZnO nanorods ranges from 440 nm to $1 \mu\text{m}$ and the diameter varies from 54 to 82 nm [54]. Compared to the photocurrent of 16 mA cm^{-2} from PSC based on the TiO_2 nanorods, an optimized PSC based on $1 \mu\text{m}$ ZnO nanorods MPSC exhibited a J_{SC} of 20.9 mA cm^{-2} , due to the much faster electron collection ratio. Three different coating solutions (the clear solution, the colloidal solution, and the nano-powder dispersed solution) were prepared for making the seed layers [53]. Vertically aligned ZnO nanorods were grown on the colloidal-based seed layer, while tilted nanorods were obtained on the solution- and powder-based seed layers. The highest V_{OC} was obtained from the solar cells with the ZnO nanorods grown on the colloidal seed layer as the combination resistances at the seed layer contact and the ZnO nanorod/perovskite interface were increased by the colloidal coating.

Other 1D structure ETL, such as ZnO nanocolumnar, TiO_2 nanohelices were reported as well. Ramos *et al.* [55] fabricated ZnO nanocolumnar films and applied them into

MPSC. However, a low PCE of 4.8% was obtained, which was ascribed to a high recombination rate and a poor injection from the absorber into this semiconductor. A TiO₂ nanohelices nanostructure was developed by Lee *et al.* [56]. This material was applied into PSC and showed an improved PCE of MPSC due to the larger contact area between the perovskite and TiO₂, leading to higher charge injection efficiency.

Besides materials with 1D nanostructure, materials with 2D nanostructure were also explored as ETL in MPSC. PSCs with these TiO₂ nanoparticle, 1D and 2D nanostructured scaffold are summarized in Fig. 5. Han's group applied TiO₂ 2D nanosheets with high reactivity of (001) facets in a hole-conductor-free fully printable MPSC [57]. The PCE of up to 10.64% was obtained with the TiO₂ nanosheet-based MPSC, because of the improved interfacial properties between the perovskite and the electron collector.

The pores of normal mesoporous ETL are introduced by the combustion of binding materials and have a random mesostructure, while, the organized geometry can be obtained by templating method. Sarkar *et al.* [58] prepared a

well-aligned mesoporous TiO₂ with various pore sizes using block copolymers as a sacrificial template. By using this organized TiO₂ as ETL in MPSC, a superior performance was shown in the mesoporous layers with bigger pores, which may be attributed to the easier filling of perovskite by bigger pore sizes.

Chen *et al.* [59] demonstrated a multifunctional inverse opal-like TiO₂ ETL by a simple polystyrene-assisted method for efficient hybrid perovskite solar cell. The novel structure of TiO₂ film enables excellent light manipulation ability and light harvesting efficiency, which improves the J_{SC} of solar cells. The inverse opal-like TiO₂ based PSC yields a best PCE of 13.11%, higher than that of the conventional P25 mesoporous layer based PSC (11.00%).

SCAFFOLD INTERFACE ENGINEERING

To improve the electron extraction and injection is an important approach to enhance the efficiency of PSCs. Two major processes electron extraction and injection occur at the ETL/perovskite layer interface. Therefore, the properties of this interface have an important influence on the device performance. Much effort has been devoted to the

Figure 5 Summary of the published representative results of MPSC performance parameters with different scaffold nanostructures. (The cell configuration is FTO/compact-TiO₂ (or ZnO)/scaffold/MAPbI₃(or FAPbI₃)/spiro-OMeTAD/Au (or Ag) without specification, where marked with * is FTO/compact-TiO₂/scaffold/MAPbI₃/C).

modification of the ETL/perovskite interfaces and a deeper understanding of interface phenomena and exploration was reported [60–62]. Here, we summarized recent progress of n-type metal-oxides scaffold interface engineering in MPSCs.

An ultrathin inorganic passivation layer is introduced into the ETL/perovskite interface. This ultrathin layer will not affect the forward electron transport, but can prevent the electrons in ETL from recombining with holes left in the perovskite layer. TiO_2 is a common passivation material adopted to modify the surface of scaffold, which can be made by atomic layer deposition (ALD), TiCl_4 -treatment, or other methods.

ALD is capable of depositing ultrathin conformal pinhole free oxide layers on high aspect ratio structures (length to diameter of the material or pore), which leads to an overall reduction in the passivation layer film capacitance, displaying a potential for devices with higher V_{OC} . Grätzel's group deposited TiO_2 over-layer on the mesoporous TiO_2 nanoparticle films with different thicknesses (0–4 nm) [63]. They found that a mere 2 nm ALD overlayer on the top of the mesoporous film was sufficient to block the back reaction both from FTO and ETL resulting in an efficiency of 11.5%. After that, Mali *et al.* [64] adopted the same method to modify TiO_2 nanorod arrays for MPSCs. By control of ALD TiO_2 thickness, the champion cell with 4.8 nm ALD TiO_2 demonstrated a PCE of 13.45% with $J_{\text{SC}} = 19.78 \text{ mA cm}^{-2}$, $V_{\text{OC}} = 0.945 \text{ V}$, and $\text{FF} = 0.72$, which is much higher than the TiCl_4 -treated TiO_2 nanorods (~9%) MPSC. However, TiCl_4 treatment was adopted to modify WO_3 and SnO_2 to suppress the charge recombination at the ETL/perovskite interface by Zhu *et al.* [28] and Mahmood *et al.* [29] respectively. By coating a thin TiO_2 barrier layer on the mesoporous SnO_2 single crystals, a PCE of 8.54% was achieved compared to 3.76% from the untreated device. Through the adoption of TiCl_4 treatment of the nanostructured WO_3 , the resulted MPSCs yields an efficiency of 11.24%, 9.01%, 6.08% for devices compared to the untreated WO_3 nanosheet, nanorods, nanoparticle based devices with efficiency of 3.8%, 3.27% and 2.14%, respectively. Park's group fabricated a TiO_2 monolayer on the surface of ZnO nanorods by $(\text{NH}_4)_2\text{TiF}_6$ treatment, leading to an improved V_{OC} and FF with a PCE of 14.35% [53]. By hydrothermal method, vertically aligned high aspect ratio ZnO nanorods with TiO_2 shell were fabricated by Mahmood *et al.* [65]. Using this ZnO nanorods (1 μm in length) materials as ETL achieves a 15.3% efficient PSC, where the high aspect ratio heterostructured ZnO/ TiO_2 promotes the perovskite infiltration and the TiO_2 shell reduces the re-

combination rate, leading to a superior light harvesting capability.

CdS has a much lower electrical mobility ($0.06\text{--}0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) than ZnO [66]. It was adopted to modify the surface of ZnO by Ogomi *et al.* [67] for the first time in 2014. The ZnO nanorods act as the main acceptor and transporter, and the CdS shell acts as additional absorption contribution, which passivates the ZnO surface defects for a high V_{OC} , reduces the interfacial charge recombination, and eliminates the perovskite decomposition.

Besides TiO_2 and CdS, the passivation layers could also be insulating materials, such as Cs_2CO_3 , MgO , Al_2O_3 and Y_2O_3 . Cs_2CO_3 has been employed as a surface modification material for MPSCs by Dong *et al.* [68]. However, the surface modification did not affect a lot on the crystal of the perovskite layer. With the optimized modifying process, 14.2% PCE was obtained, enhanced by nearly 20% compared with the control devices due to the improved electron transport and retarded back recombination. Han *et al.* [69] used MgO to modify the surface TiO_2 nanoparticle. The recombination times for the MgO -coated TiO_2 -based PSC about three times longer than those of plain TiO_2 based solar cells. A passivation layer of Al_2O_3 or Y_2O_3 was inserted between TiO_2 ETL and perovskite layer to remove surface traps of the porous layer by Ogomi *et al.* [67]. Both passivations were effective in increasing the efficiency of the solar cell.

Interfacial modification can also be modified with materials with superfast charge mobility as an electron acceptor. In Zhu *et al.*'s work, they used an ultrathin graphene quantum dots layer to modify the surface TiO_2 ETL in MPSC [70]. An efficiency improvement of PSC from 8.81% to 10.15% was observed, where the graphene served as a superfast bridge to facilitate the electron injection from perovskite into TiO_2 , leading to a significantly enhanced photocurrent and PCE. Al-doped ZnO (AZO) with a higher conduction band, faster electron mobility and higher electron density than ZnO was used to modify ZnO nanorods by Dong *et al.* [71]. After surface modification, the average PCE of the PSCs with ZnO nanorods ETL was improved from 8.5% to 10.07%, because of the suppressed recombination at the $\text{ZnO}/\text{CH}_3\text{NH}_3\text{PbI}_3$ interface. Abrusci *et al.* [72] used fullerene functionalized mesoporous TiO_2 to achieve an 11.7% MPSC. The fullerene acts as an electron acceptor but inhibits further electron transfer into the TiO_2 mesostructure due to energy level misalignment and poor electronic coupling. Thermalized electrons from the fullerene are then transported through the perovskite phase, allowing a reduction of energy loss.

ZnO-based photovoltaics have a higher recombination rate than TiO₂-based ones, but surface modification of ZnO could be adopted to suppress the recombination rate. The highest PCE of the ZnO-based MPSC so far was obtained by Mahmood *et al.* [32]. By combining mesoscale control with doping and surface modification, they successfully fabricated N doped ZnO based PSC with a PCE up to 16.1%. The N doped ZnO nanorod array, prepared from a low-temperature solution-process, exhibits higher nanorods aspect ratio, enhanced electron density, and substantially reduced work function than conventional ZnO nanorods. The coating of polyetherimide (PEI) monolayer on the N doped ZnO nanorod arrays results in a favorable work function shift and altogether leads to the significant boost in efficiency from <10% up to >16%.

Many organic self-assembled monolayers were inserted between ETL and perovskite to modify the ETL/perovskite interface. Liu *et al.* [8] introduced an organic silane self-assembled monolayer between the TiO₂ and MAPbI₃, resulting in optimized interface band alignments and enhanced charge lifetime. The average PCE of HTL-free, fully printable MPSCs based on a carbon counter electrode is improved from 9.6% to 11.7%, with a highest efficiency of

12.7%. Li *et al.* [73] modified the TiO₂ ETL with alkylphosphonic acid ω -ammonium chlorides. The phosphonic acid ammonium additive acts as a crosslinker between TiO₂ and perovskite through strong hydrogen bonding of the $-\text{PO}(\text{OH})_2$ and $-\text{NH}_3^+$ terminal groups to the perovskite surface. The additives facilitate the incorporation of the perovskite within a mesoporous TiO₂ scaffold, as well as the growth of a uniform perovskite layer at the surface, enhancing the material's photovoltaic performance from 8.8% to 16.7% as well as its resistance to the moisture. Ogomi *et al.* [74] applied $\text{HOCO-R-NH}_3^+\text{I}^-$ monolayer between the surface of porous metal oxide and the perovskite. A PCE of 12% was achieved for the cells fabricated at optimized conditions. This increase of the efficiency was explained by the retardation of charge recombination, and better perovskite crystal growth. Some other organic monolayers were used to modify the surface of scaffold through the influence of the morphology and growth of perovskite, such as glycine, thiols and 4-aminobenzoic acid, yielding positive effects on cell performance [75–77]. A summary of the published representative results of MPSCs' performance parameters with different scaffold interface modification is listed in Table 2.

Table 2 Summary of the published representative results of MPSCs' performance parameters with different scaffold interface modification

Scaffold interface engineering	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	Ref.
TiO ₂ nanoparticle with TiO ₂ modification	17.6	1.00	67	11.5	[63]
Mesoporous SnO ₂ single crystals with TiO ₂ modification	17.2	0.80	62	8.5	[28]
ZnO nanorod with TiO ₂ modification	22.0	1.00	70	15.4	[65]
ZnO nanorods with TiO ₂ modification	19.4	1.06	70	14.4	[53]
WO ₃ nanorods with TiO ₂ modification	17.0	0.87	76	11.2	[29]
TiO ₂ nanoparticle with Cs ₂ CO ₃ modification	21.3	1.03	65	14.2	[68]
TiO ₂ nanoparticle with MgO modification	20.0	0.89	71	12.7	[69]
TiO ₂ nanoparticle with Y ₂ O ₃ modification ^{a)}	16.6	0.79	71	7.5	[67]
TiO ₂ nanoparticle with Al ₂ O ₃ modification ^{a)}	12.6	0.83	71	7.0	[67]
TiO ₂ nanoparticle with graphene modification	17.1	0.94	64	10.2	[70]
ZnO nanorod with Al doped ZnO modification	19.8	0.90	60	10.7	[71]
TiO ₂ nanoparticle with C60 modification ^{a)}	19.6	0.84	72	11.7	[72]
TiO ₂ with organic silane modification ^{b)}	19.5	0.87	75	12.8	[8]
TiO ₂ nanoparticle with alkylphosphonic acid ω -ammonium chlorides modification	22.0	1.00	75	16.6	[73]
TiO ₂ nanoparticle with $\text{HOCO-R-NH}_3^+\text{I}^-$ modification	19.2	1.00	62	12	[74]
TiO ₂ with glycine modification	16.2	0.98	60	9.5	[75]
TiO ₂ nanoparticle with HOOC-Ph-SH modification	20.7	1.02	66	14.7	[76]
TiO ₂ nanoparticle with 4-aminobenzoic acid modification	22.3	0.92	52	10.6	[77]
ZnO nanorod with CdS modification ^{c)}	7.23	1.04	57	4.3	[78]
N doped ZnO nanorods with PEI modification	22.1	1.00	74	16.3	[32]

The cell configuration is FTO/compact layer/scaffold/MAPbI₃/spiro-OMeTAD/Au (or Ag) without specification. a) FTO/compact-TiO₂/scaffold/MAPbI₃-xCl_x/spiro-OMeTAD/Au; b) FTO/compact-TiO₂/scaffold/MAPbI₃/C; c) ITO/compact-ZnO/scaffold/poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene)/MAPbI₃/PEDOT:PSS/Au.

CONCLUSIONS

In this review, we summarized the recent results of n-type metal-oxide electron transport layer in MPSCs. Three aspects were discussed: anatase TiO₂ is still the dominant material used as ETL in MPSCs, although various novel materials, such as ternary metal-oxides, doped materials, nanocomposites materials, were adopted to replace it; the traditional electron transport layer is anatase TiO₂ nanoparticle with pores introduced by the combustion of binders in paste, while ETL with 1D or 2D nanostructures are attempted and showing some promising results in MPSCs; another way to modify the ETL is interface engineering, which greatly affects the morphology of perovskite and further affects the performance of MPSCs. In the device of MPSCs, careful design of the active metal-oxides scaffold should take material, nanostructure and interface engineering of the ETL and their interrelation into consideration to achieve a high efficient perovskite solar cells.

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n型金属氧化物电子传输层在介观钙钛矿太阳能电池中的研究

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摘要 为了满足日益增长的世界能源需要,有机-无机卤化物材料制备的钙钛矿太阳能电池因成本低廉和转换效率高,受到光电材料研究学术领域的高度重视. 其获得公证的光电转换效率在短时间内由2009年的3.8% 提高到2016年的22.1%. n型电子传输层,作为介观钙钛矿太阳能电池的重要组成部分,不仅作为钙钛矿晶体生长的骨架层,还为钙钛矿的激发电子注入提高传输通道. 因此,本文简要评述了介观钙钛矿太阳能电池的最新进展,重点介绍了n型金属氧化物电子传输层在介观钙钛矿太阳能电池中的研究近况,主要包括:骨架的材料,骨架的形貌以及骨架同钙钛矿材料层的界面,同时还探讨了这些n型金属氧化物电子传输层的改性和修饰对介观钙钛矿太阳能电池性能的影响.