

Progress on Electron Transport Layers for Perovskite Solar Cells

^{*1,2}Yusuf, A. S., ³Ramalan, A. M., ¹Abubakar, A. A. and ¹Mohammed, I. K.

¹Department of Physics, Federal University of Technology, P.M.B 65, Minna, Nigeria.

²Department of Physics and Astronomy, Auckland University of Technology, New Zealand.

³Department of Physics, University of Abuja, P.M. B. Abuja, Nigeria.

*Corresponding author's email: ayusuf@futminna.edu.ng

ABSTRACT

The photovoltaic industry is very interested in designing and developing next-generation device architectures using organic-inorganic perovskite hybrid solar cell materials. In fact, perovskites represent one of the most promising materials for high efficiency, low-cost solar cells. This is most apparent in the power conversion efficiency of perovskite solar cells (PSCs) going from 3.8 to 24.2 % in recent years. One of the primary challenges of developing PSC's however is the realization of an appropriate electron transport layer. As such, this review focuses on recent developments in the electron transport layer (ETL) of perovskite solar cells. It examines and summarises designs, electron transport layers and perovskite active layers for efficient perovskite solar cells. The performance and stability issues with organic-inorganic halide perovskite solar cells are also discussed with some recommendations for additional research on the ETL and perovskite active layer were offered.

Keywords:

Active layer,
Electron transport layer,
Mesoporous,
Perovskite solar cell

INTRODUCTION

The solar energy sector is particularly interested in organic-inorganic perovskite hybrid solar cells for the design and development of next-generation photovoltaic systems to meet the current demand for inexpensive and environmentally friendly electricity. In this respect, organic-inorganic hybrid perovskites are promising materials for highly efficient and inexpensive solar cells. This is best illustrated by the photovoltaic conversion efficiency of perovskite solar cells (PSCs) having increased in recent years from 3.8 to 24.2 % (Kojima et al., 2009; Tang et al., 2019). This is attributable to the fact that the materials offer excellent light absorption with a small bandgap, extended charge carrier lifetimes, high carrier mobility, long diffusion lengths and also their excellent charge transport properties (Ahn et al., 2015; Chen et al., 2015).

In a generic sense, the crystal structure of a perovskite takes the form AMX_3 as shown in Figure.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" is a halide anion (e.g., Br^- , I^- , Cl^-) or a mixture of them. In this respect, the development of PSCs represents a succession to work in the field of dye-sensitized solar cells. In fact Methyl-ammonium lead iodide and bromide ($MAPbBr_3$ and $MAPbI_3$) were utilized as sensitizers in dye-sensitized solar cells by Miyasaka et al. in 2006 and 2009, with their devices achieving an efficiency of 3.13 % and 3.81 % respectively (Kojima et al., 2009; Lachore et al., 2021). Additionally, in 2011, Park et al. showed that $CH_3NH_3PbI_3$ quantum dots (QD) placed on a nanocrystalline TiO_2 surface created a highly effective quantum-dot sensitive solar cell, with a power conversion efficiency of 6.5%. However, owing to the device's unstable design, 80% of the sensitizer deteriorated after 10 min (Im et al., 2011). Hence, to increase the conversion efficiency, Spiro-OMeTAD was substituted with a solid hole transport layer for the liquid electrolyte in a dye-produced solar cell with a TiO_2 electron transport layer.

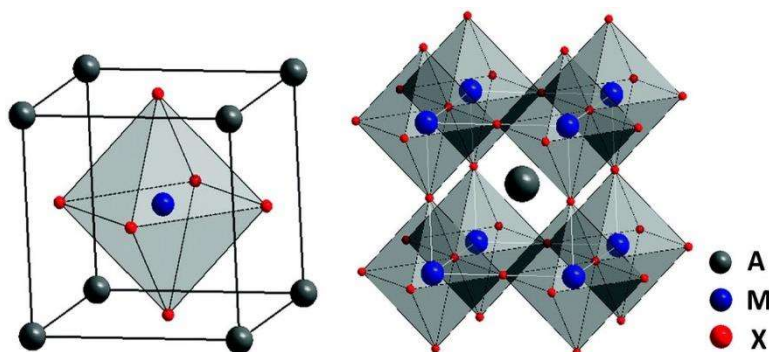


Figure 1: Configurations of cubic perovskite crystals with the AMX_3 general formula (Liu et al., 2015) Reproduced from (Liu, X., et al., 2015) with permission from the Royal Society of Chemistry.

More recently (2,2',7',7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'spirobifluorene) has also been utilized with a photovoltaic conversion efficiency 9.7% being achieved (Kim et al., 2012). These developments have led to planar heterojunction perovskite solar cells, with TiO_2 as the electron transport layer, being developed by both vapor deposition and solution treatment methods (Liu, Johnston, & Snaith, 2013). Without nanostructures and by substituting the conventional one-step solution approach, the power conversion efficiencies of the methods were 15.4% and 8.6%, respectively.

These studies led to the development of the first organic-inorganic halide perovskite, $CH_3NH_3PbCl_3$ -XIX (Lee et al., 2012). This performed well as a light absorber when compared to the typical $CH_3NH_3PbI_3$ used in many PSCs. Furthermore, it was shown that switching to a nano porous Al_2O_3 scaffolding from TiO_2 increased efficiency 7.6 to 10.9%.

Given the desire to capture the greatest amount of visible light, scientists have been developing more effective perovskite photon-absorbing materials. This work has aimed to improve the synthesis mechanism and procedures whilst also addressing the electrical structure of the photon-absorbing perovskite active layer. Owing to their influence on the ability of the cell to capture photogenerated carriers, electron and hole transport layers have attracted considerable research attention.

Specifically, efforts have been made to increase the effectiveness of collecting photogenerated charge carriers. However, in doing this, proper consideration must be given to the interface between the photon absorption layer, electron transport layer (ETL), and hole transport layer (HTL) (Agha & Algwari, 2021; Yang et al., 2016) such that photogenerated electrons migrate from the perovskite photon active layer to the contact electrode, whilst blocking the migration of holes to the counter electrode.

The type of ETL being utilized, affects these events, and can be used to improve the charge carrier separation kinetics and decrease electron-hole recombination at the interface (Ahn et al., 2015; Ke et al., 2015). Given the significance of this, this review paper provides a brief overview of the current developments in PSC ETLs, and the dynamics of photogenerated carriers, and how the current development of PSCs may affect the stability and effectiveness of inorganic-organic halide perovskite solar cells.

Perovskite solar cells

Device architecture

As noted previously, perovskite solar cells have a shared history with other similar device designs, such as dye-sensitized solar cells. In this sense, mesoporous, planar, and inverted planar (as illustrated in Fig. 2) are the three primary architectures of perovskite solar cells.

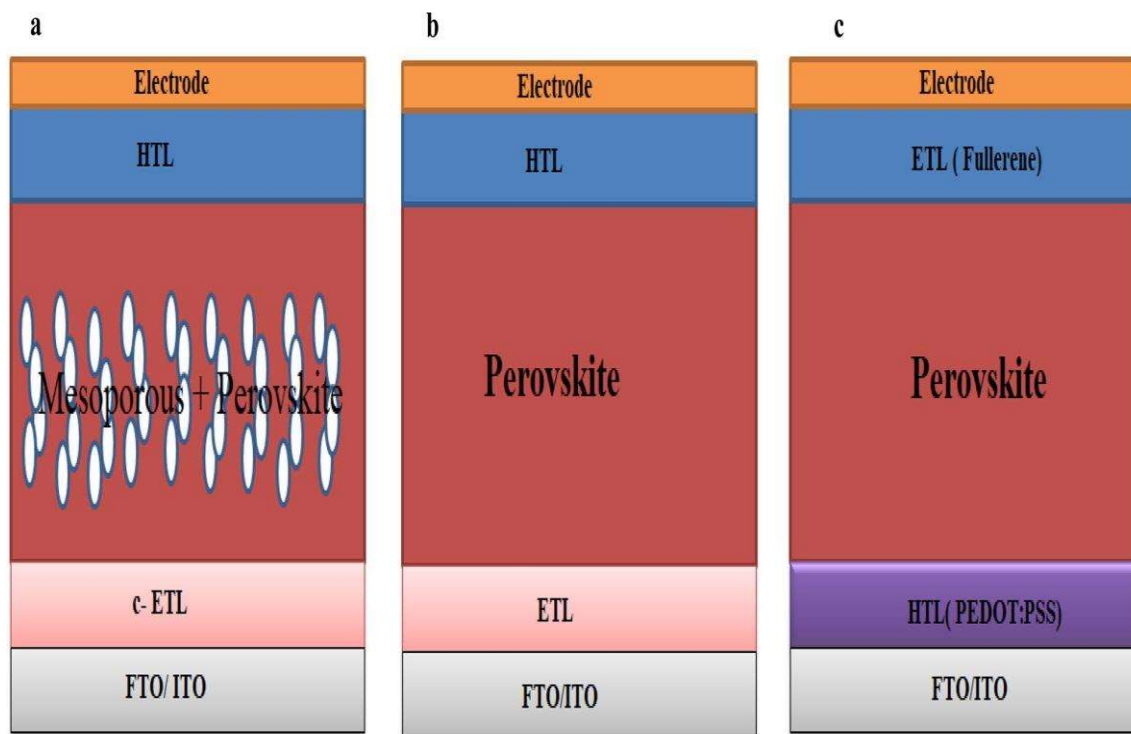


Figure 2: Various device architectures of perovskite solar cells: **a** mesoporous, **b** planar, and **c** inverted planar device (Pham et al., 2020). Reproduced from (Liu, X., et al., 2015) with permission from the Royal Society of Chemistry.

Mesoporous perovskite solar cells

Mesoporous materials have been extensively investigated and exploited owing to their high porosity and substantial specific surface area. These materials possess large surface area, that makes it possible to capture more photons per unit area. Furthermore, they lower the rate of recombination, and increase the efficiency of charge collection in solar-cell devices. As one example, methyl-ammonium lead iodide $\text{CH}_3\text{NH}_3\text{PbI}_3$ and bromide $\text{CH}_3\text{NH}_3\text{PbBr}_3$ were used as sensitizers on mesoporous TiO_2 to introduce mesoscopic perovskite solar cells. This delivered efficiencies of 3.82 % and 3.13% with an organic liquid electrolyte (Kojima et al., 2006).

Similarly, Kim et al. investigated perovskite mesoscopic solar cells employing a solid hole transportation layer

(Spiro-OMeTAD) with TiO_2 as the electrolyte transport layer to avoid rapid performance deterioration caused by the dissolution of the perovskite material into the liquid electrolyte (Kim et al., 2012). Although TiO_2 compact thin films (ETL) have been widely used, mesoporous materials, including ZnO , SiO_2 , Al_2O_3 , and ZrO_2 are frequently used in perovskite mesoscopic solar cells. These mesoscopic perovskite solar cells have reported power conversion efficiencies of more than 20% to date (Guo et al., 2020; W. Sun, K.-L. Choy, & M. Wang, 2019; Zhang et al., 2020), and Table 1 provides a summary of perovskite solar cells made from distinct mesoporous perovskite photon-absorbing layers with varying ETL.

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
$\text{MAPbI}_3(\text{CH}_3\text{NH}_3\text{PbI}_3)$	c- TiO_2 /mp- TiO_2	1.04	20.44	15.51	(Kojima et al., 2009)
$(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Cs}_{0.05}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$	mp- TiO_2 - $\text{Ba}(\text{OH})_2$	1.09	20.81	17.53	(Lachore et al., 2022)
$\text{MAPbI}_3(\text{CH}_3\text{NH}_3\text{PbI}_3)$	MgTiO_3 /mp- TiO_2 hole-conductor-free	with 0.95	14.05	22.62	(Lee et al., 2012; Liu & Kelly, 2013)
$\text{MAPbI}_3(\text{CH}_3\text{NH}_3\text{PbI}_3)$	BI- Mg-SnO_2 /mp- SnO_2	1.112	22.80	19.12	(Li et al., 2015)

MAPbI ₃ (CH ₃ NH ₃ PbI ₃)	c-TiO ₂ /mp-Sb doped SnO ₂	1.10	23.81	20.1	(Niu, Guo, & Wang, 2015)
(FA _{0.83} MA _{0.17}) _{0.95} CS _{0.05} Pb(I _{0.9} Br _{0.1}) ₃	c-SnO ₂ /mp-Sc ³⁺ doped brookite TiO ₂	1.145	23.63	21.75	(Niu et al., 2013)
CH ₃ NH ₃ PbI _{3-x} Cl _x / (GO or m GO)	c-TiO ₂ / mp-TiO ₂	0.85/0.93	20.49/ 24.43	8.96/13.25	(Pan et al., 2020)
MAPbI ₃ (CH ₃ NH ₃ PbI ₃)	PET/ITO/SnO ₂ /meso-TiO ₂	1.036 ± 0.011	±20.70 ± 0.28	14.07 ± 0.58 (14.8)	(Pham et al., 2020)
MAPbI ₃ (CH ₃ NH ₃ PbI ₃)	c-TiO ₂ /mp-TiO ₂	1.059	19.62	15.12	(Qiang et al., 2020)
(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15}	c-TiO ₂ /GQD-x/mp- TiO ₂	1.08	24.92	20.45	(W. Sun, K. L. Choy, & M. Wang, 2019)
MAPbI ₃ (CH ₃ NH ₃ PbI ₃)	O-mp-TiO ₂	1.13	22.4	19.7	(Tang et al., 2019)
CH ₃ NH ₃ PbI _{3-x} Br _x	c-TiO ₂ /mp-TiO ₂	1.141	23.42	20.43	(Tomulescu et al., 2020)
MAPbI _x Cl _{3-x}	mp-Al ₂ O ₃ /mp-TiO ₂	1.069	20.78	16.84	(Zheng et al., 2020)
CH ₃ NH ₃ PbI _{2.6} Cl _{0.4}	c-TiO ₂ /mp-TiO ₂	1.045	20.1	12	(Yang et al., 2016)
MAPbI _{3-x} Br _x	Bi-TiO ₂	1.03	23.55	18.20	(Yu et al., 2022)
(FAPbI ₃) _{1-x} (MAPbBr ₃) _x	/H ₃ PW ₁₂ O ₄₀ ·nH ₂ O/mp-TiO ₂ c-Nb ₂ O ₅ /m-Nb ₂ O ₅	1.04	23.2	17.4	(Zhang et al., 2020)

Scaffold materials in perovskite solar cells

When developing perovskite solar cell architectures, it is important to consider the role of scaffolding materials. A scaffold material acts as a support layer and frame for perovskite solar cells but is unable to transport electrons into the cells. Smooth electron injection into SiO₂ and ZrO₂ is prevented by materials with large bandgaps and conduction band borders, which are significantly higher than those of the perovskite layer. Consequently, the excited electrons spend more time in the conduction band of the perovskite layer. Perovskite solar cells have been reported to use TiO₂, ZnO, SiO₂ (Hwang et al., 2014), Al₂O₃ (Niu, Guo, & Wang, 2015), Nb₂O₅, and ZrO₂ (Bi et al., 2013b) as scaffold materials, with a PCE of approximately 10%.

A helpful method for increasing the short-circuit current density was described in (Qiang et al., 2020). In this study an Al₂O₃ interlayer was created using a low-temperature sol-gel procedure between the Li-SnO₂ (Li⁺-SnO₂) ETL and CH₃NH₃PbI₃ layers. The Al₂O₃ layer was placed on top of the perovskite layer resulting in the power conversion efficiency increasing to 10%, whilst the device performance and stability were also enhanced. However, the weak interface-contact between the perovskite layer and carbon counter electrode caused the fill factor to decrease. In summary the Al₂O₃ layer in the device lowered the electron-hole recombination at the interface between the ETL and perovskite layers, leading to improved perovskite solar cells.

Xiong et al. also altered the interface between the electron transport layer and the perovskite active layer

in carbon-based perovskite solar cells with a hole-conductor-free associate-degree inclusion of an Al₂O₃ layer. As a result, electron-hole recombination was prevented at the interface between the ETL, the perovskite layer and the counter conductor lead. This insulating layer kept the cathode and anode separate (Xiong et al., 2018).

To examine the stability of CH₃NH₃PbI₃ and its sensitized film under moisture and sunlight, Niu et al. also employed aluminum as a post-modification material. Al₂O₃ was used to shield perovskite solar cells from moisture and UV damage, thereby increasing their stability and effectiveness. Additionally, it reduced spiro-OMeTAD and electron-hole recombination at the TiO₂ surface. Furthermore, when exposed to moisture, the Al₂O₃ modification showed better stability (Niu, Guo, & Wang, 2015).

(Dong et al., 2015) also presented a technique for interface modification utilizing extremely thin Al₂O₃ films to increase the stability of perovskite solar cells under ambient conditions. The results demonstrated that the environmental stability significantly increased without noticeably reducing their efficiency. Additionally, they used molecular structure modelling to explain the mechanisms of degradation of organic/inorganic hybrid structures and discovered that the stability of CH₃NH₃PbI₃ is significantly influenced by the hydrogen bonding interactions between the inorganic PbI₃ unit and the organic CH₃NH₃ unit.

For perovskite thin-film solar cells, Bi et al. synthesized ZrO₂ and TiO₂ as mesoporous layers using two- and

one-step deposition techniques, respectively. Two- and one-step techniques were used to compare the power conversion effectiveness of ZnO_2 and TiO_2 . The one-step and two-step procedures for TiO_2 -based solar cells were outperformed by the two-step methodology for ZnO_2 (PCE: 10.8% for ZnO_2)-based solar cells (PCE: 9.8 % for TiO_2). Consequently, at the same voltage the electron lifetime in solar cells based on ZrO_2 was greater than that in solar cells based on TiO_2 , as shown in Fig. 3 (Bi et al., 2013a).

(Inami, Ishigaki, & Ogata, 2019) described Nb_2O_5 as a scaffold layer (SL) and contrasted the ability of perovskites to remove electrons from interfaces with Nb_2O_5 and m-TiO_2 . The photoluminescence

spectroscopy results showed that the perovskite/ Nb_2O_5 interface had a greater electron-extraction capability than the perovskite/ m-TiO_2 interface, as shown in Fig. 3. They suggested relaxing the photoexcited carriers in the perovskite film, as shown in Fig. 3d. In addition to serving as an effective electron transport layer, it aided in the crystallization of the perovskite film beneath, both of which are crucial components of high-performance perovskite solar cells. Additionally, it was discovered that compared with the perovskite/ m-TiO_2 film, the perovskite layer on Nb_2O_5 exhibited fewer pinhole flaws. Consequently, the mesoporous perovskite solar cells enhanced optoelectronic characteristics, and improved photovoltaic efficiency, and stability.

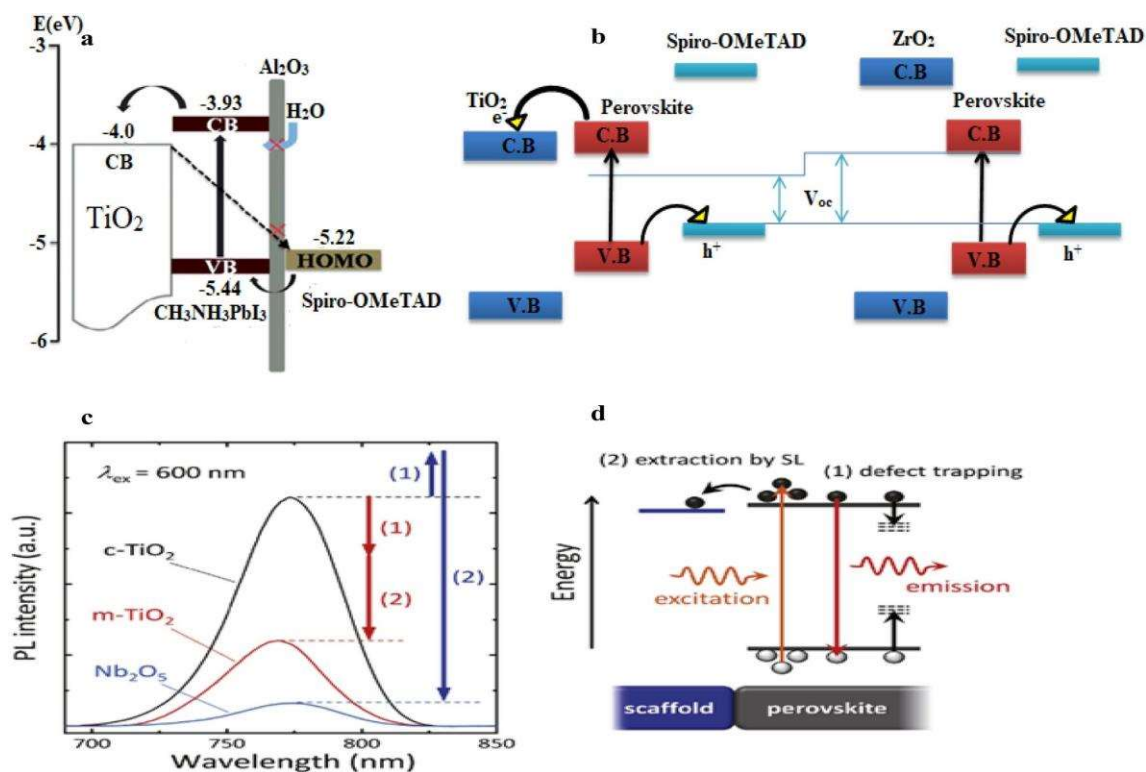


Figure 3: description of a schematic **a** graph of the device's energy levels after modification by Al_2O_3 , **b** a model for the charge separation processes and the energy levels in the two solar cell interfaces, **c** PL spectra of the perovskite films on the scaffold layers made of Nb_2O_5 (blue), mesoporous TiO_2 (red), and compact TiO_2 (black). **d** Schematic representation of the perovskite film's photoexcited carriers relaxing (Bi et al., 2013a; Inami, Ishigaki, & Ogata, 2019; Niu et al., 2013). Reproduced from (Liu, X., et al., 2015) with permission from the Royal Society of Chemistry.

(Inami, Ishigaki, & Ogata, 2019) observed mesoporous TiO_2 films with high roughness reticulated structures that could be sprayed over large surfaces in the open air. The average power conversion efficiency was between 10 and 12 % greater than devices with a spin-coated smooth surface mesoporous scaffold in PSCs with small and large active surfaces up to 1 cm^2 . The deposition of a thicker perovskite and an extension of the TiO_2 and perovskite interface, as well as improved

photogenerated charge collection and less hysteresis, were all made possible by decreasing charge losses within the most resistive component layer (Tomulescu et al., 2020).

As a scaffold for perovskite solar cells, Asl et al. examined a thin film in 2020 with mesoporous nanoparticles, nanorods, and nano-branching nanorods. However, nano-branched nanorods outperformed nanoparticles and nanorods in photovoltaic performance

because of their superior optical properties. These demonstrated excellent electron transport properties and desired light-harvesting performance, which are desirable features for boosting the efficiency of perovskite solar cells (e Asl et al., 2020).

Overall, scaffold materials are crucial in perovskite solar cells because they shield recombination electrons from the electrode and electron transport layer interfaces. Moreover, they increase the efficiency of electron extraction from the electrode to the ETL interface at the perovskite absorber layer interface.

Electron transport materials in perovskite solar cells

Overall, scaffold materials are crucial in perovskite solar cells because they shield recombination electrons from the interface between the electron transport layer and the perovskite absorber layer/electrode and increase the ability to extract electrons from the perovskite absorber layer interface to the ETL interface. Furthermore, the pinhole and fracture between the FTO substrate and the perovskite electrode are reduced (Kim, Lim, & Song, 2020).

To enhance the efficiency of perovskite solar cells it is critical to address carrier separation and reduce interface electron-hole recombination. This is influenced by ETL characteristics, including charge mobility, energy level alignment, trap states, interface, and surface shape. High charge mobility resulting from the ETL is crucial for perovskite solar cells to function properly because it promotes effective charge transfer and collection while preventing charge recombination at the interface (Pan et al., 2020; Yu et al., 2020).

Further, appropriate energy-level alignment is another factor that increases the performance of perovskite solar cells. The extraction and transmission of electrons are simplified when the ETL is properly aligned with the perovskite absorber layer. This delivers an increase in the open-circuit voltage, fill factor, and short-current density (J_{sc}) (V_{oc}). Similarly, charge extraction, transport, and recombination at the interface are important issues to be resolved in the delivery of high-efficiency PSCs. Trap states, which affect charge extraction and transport and result in a high recombination rate at the interface, are among the most important elements in ETL. As such, interface engineering can be used to enhance the electron transport layer whilst the surface morphology of the ETL can be improved to improve the device performance. Consequently, all the components contribute to determining the characteristics of these devices (Chen & Park, 2020; Yu et al., 2020).

Electron Transport Layers

Now as it has been noted the ETL has a significant role to play in the performance of an effective PSC. The electron transport layer (ETL) transfers the electrons

generated from the intrinsic perovskite layer. In effect, there are three different types of electron transport layers; the first type of electron transport layer is an n-type material, which only has the function of transferring electrons. For example, mesoporous TiO_2 normally plays an important role in PSCs. In conventional PSCs, a blocking layer, normally between the electron transport layer and conductive glass, is used. This prevents the electrons from being recaptured by the hole-transport layer. Nanostructured materials, such as nanotubes, nanorods, nanowires, and nanocrystalline mesoporous layers, are normally used in this type of electron transport layer (Burschka et al., 2013; Qin et al., 2015; Salado et al., 2017).

The second type of electron transport layer still has the same function; however, it is for inverted-structure PSCs. A blocking layer is normally placed between this layer and the metal back-contact. Based on the morphology, this layer is normally prepared as a dense thin film. This is because the perovskite was deposited beneath this layer; thus, a planar structure can have the maximum contact area on the perovskite/electron transport layer interface. Organic hole electron transport layers such as organic [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) can be attributed to this type of electron transport layer (Fu et al., 2015; Wang, 2018).

The third type of electron transport layer is a bifunctional layer that functions as both an electron transport layer and blocking layer. This is normally a thin film formed between the perovskite layer and conducting glass. For example, SnO_x in planar PSCs functions in this manner (Zhang et al., 2017). This requires the layer to be dense enough to maximize the shunt resistance of the device and thin enough to reduce the series resistance. In this respect, there are three different types of materials in the electron transport layer: inorganic materials, organic materials, and polymers. An ideal electron transport material has a conduction band that aligns with the conduction band edge of perovskite materials, with a faster electron transfer time than its recombination speed with the hole transport layer, and uniform contact with perovskite materials. Moreover, in conventional PSCs, the ETL should be transparent to maximize the incident photons captured by perovskite materials (Mahmood et al., 2018).

One of the most frequently applied ETL materials is mesoporous anatase TiO_2 . The application of this material in PSCs was inspired by dye-sensitized solar cells, which typically use this material. The size of the nanocrystal TiO_2 was approximately 20-30 nm, and the pore size was above 50 nm. This is done, as the perovskite band edge typically aligns with the conduction band of the anatase TiO_2 . The nanocrystal and mesoporous structure of the film ensures high loading of perovskite materials (Burschka et al., 2013).

However, the necessity of a high perovskite loading is questionable because of the ultrahigh absorption coefficient of the perovskite materials (Song et al., 2015).

In this vein, several studies have reported the efficiency of PSCs using mesoporous TiO_2 as an ETL (Burschka et al., 2013; Jeon et al., 2014). To further improve the electron conductivity, several groups have applied Li doping of TiO_2 and has been shown to improve the conductivity of the ETL resulting in efficiencies of 20% (Giordano et al., 2016). However, there are several problems associated with mesoporous TiO_2 in PSCs. It has a high annealing temperature (450–500 °C), which limits its application to flexible substrates, and, with more input energy, the fabrication cost increases. However, perovskite/ TiO_2 interfaces are unstable under

intense light, thus TiO_2 can act as a catalyst to decompose the organic components in perovskite materials (Bryant et al., 2016).

Mesoporous Al_2O_3 ETLs have been applied as a substitute for TiO_2 , with higher stability and comparable efficiency, even though its band edge does not align with perovskite materials. The authors of one study (Lee et al., 2012) proposed a mechanism in which the electrons of the perovskite do not need to cross the bulk of the ETL and can be transferred to the surface state of Al_2O_3 . In addition, SnO_x and ZnO have also been used in PSCs. Both can be prepared in the conventional device and inverted device with improved stability and lower fabrication temperature (Ke et al., 2015; You et al., 2016) Figure 4 listed several materials for the ETL in PSCs.

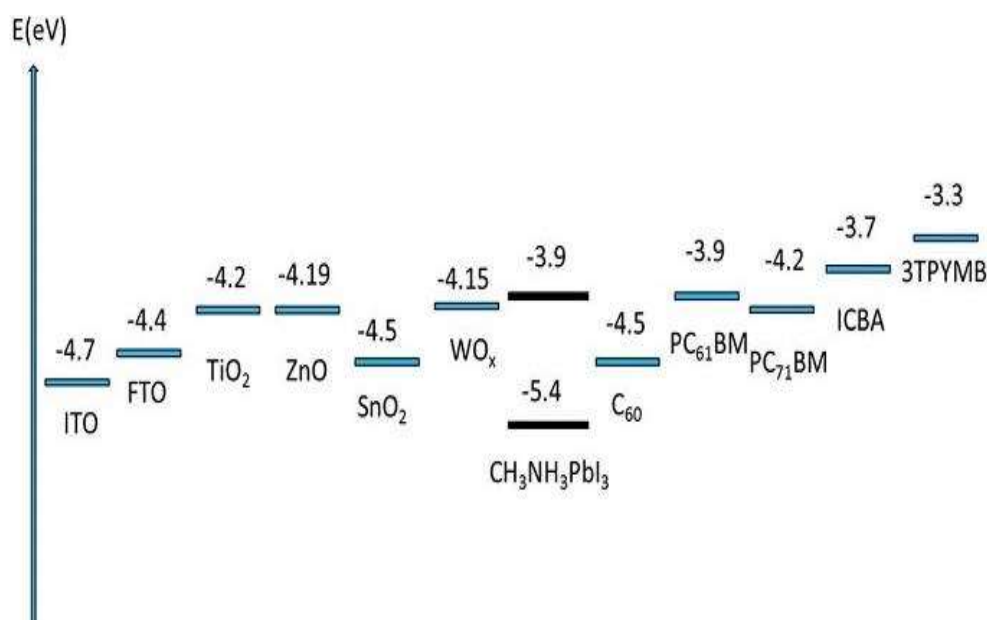


Figure 4: Materials for ETL in PSCs showing conduct band minimum/LUMO levels (Yang et al., 2016). Reproduced from (Liu, X., et al., 2015) with permission from the Royal Society of Chemistry.

For high-efficiency solar cells with a PCE of 20%, researchers (W. Sun, K.-L. Choy, & M. Wang, 2019) have also employed 20–30 nm thick SnO_2 (rather than TiO_2) in the planar regular structure (n-i-p) and a 20–30 nm compact TiO_2 layer for the mesostructured. They showed that significantly thicker layers (of 152 nm), corresponded with the highest efficiency achieved (PCE of 18.32 %). However, the thickness of the layers in ALD layer deposition technology might be substantially lower. Conversely, Lu and colleagues (Lu et al., 2015) showed that the optimal thickness for the ALD technique is considerably smaller, equal to 10 nm (PCE of 13.6%). This suggests that the ETL may be very thin but must also be of good quality.

CONCLUSION

In perovskite solar cells, charge transport layers may act as n-type to connect the halves in a p-n junction. They may also reduce surface recombination at the interface, channel the current to the metal electrode, and enable the maximum amount of incoming light to flow through and reach the absorber layer. In this review, we discuss efforts to enhance the PCE using an ETL, as well as the interface between the ETL and perovskite absorber layer. Numerous metal oxides have been studied and used in perovskite solar cells, including TiO_2 , ZnO , SnO_2 , WO_x , and fullerene. The reduced charge carrier recombination at the surface, which improves the ability of the layer to conduct current, may be the reason for the better charge collection performance utilizing ETL.

Furthermore, improving charge extraction and transportation depends on the interface between the charge transport layers, and the perovskite active layer changes with useful self-assembled monolayers (SAMs). In addition, the limiting charge recombination suggests improved performance and stability of the perovskite solar cell apparatus. Therefore, carefully selecting ETL and interface design are required to utilize the greatest amount of visible-light-generated charge carriers in perovskite solar cells. One finding from the review, was that there has been little discussion on how doping affects the characteristics of ETL in perovskite solar cells and this may be an area of future exploration.

FUNDING

This work was funded by the Tertiary Education Trust Fund (Tetfund) Nigeria.

ACKNOWLEDGEMENTS

We express our heartfelt gratitude to Tetfund Nigeria for supporting this study.

REFERENCES

Agha, D. N. Q., & Algwari, Q. T. (2021). The influence of the interface layer between the electron transport layer and absorber on the performance of perovskite solar cells. *IOP Conference Series: Materials Science and Engineering*,

Ahn, N., Son, D.-Y., Jang, I.-H., Kang, S. M., Choi, M., & Park, N.-G. (2015). Highly reproducible perovskite solar cells with average efficiency of 18.3% and best efficiency of 19.7% fabricated via Lewis base adduct of lead (II) iodide. *Journal of the American Chemical Society*, *137*(27), 8696-8699.

Bi, D., Moon, S.-J., Häggman, L., Boschloo, G., Yang, L., Johansson, E. M., Nazeeruddin, M. K., Grätzel, M., & Hagfeldt, A. (2013a). Using a two-step deposition technique to prepare perovskite (CH₃NH₃PbI₃) for thin film solar cells based on ZrO₂ and TiO₂ mesostructures. *RSC advances*, *3*(41), 18762-18766.

Bi, D., Moon, S.-J., Häggman, L., Boschloo, G., Yang, L., Johansson, E. M., Nazeeruddin, M. K., Grätzel, M., & Hagfeldt, A. (2013b). Using a two-step deposition technique to prepare perovskite (CH₃NH₃PbI₃) for thin film solar cells based on ZrO₂ and TiO₂ mesostructures.

Bryant, D., Aristidou, N., Pont, S., Sanchez-Molina, I., Chotchunangatchaval, T., Wheeler, S., Durrant, J. R., & Haque, S. A. (2016). Light and oxygen induced degradation limits the operational stability of methylammonium lead triiodide perovskite solar cells.

Energy & Environmental Science, *9*(5), 1655-1660. <https://doi.org/10.1039/c6ee00409a>

Burschka, J., Pellet, N., Moon, S. J., Humphry-Baker, R., Gao, P., Nazeeruddin, M. K., & Grätzel, M. (2013). Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature*, *499*(7458), 316-319. <https://doi.org/10.1038/nature12340>

Chen, J., & Park, N.-G. (2020). Materials and methods for interface engineering toward stable and efficient perovskite solar cells. *ACS Energy Letters*, *5*(8), 2742-2786.

Chen, W., Wu, Y., Yue, Y., Liu, J., Zhang, W., Yang, X., Chen, H., Bi, E., Ashraful, I., & Grätzel, M. (2015). Efficient and stable large-area perovskite solar cells with inorganic charge extraction layers. *Science*, *350*(6263), 944-948.

Dong, X., Fang, X., Lv, M., Lin, B., Zhang, S., Ding, J., & Yuan, N. (2015). Improvement of the humidity stability of organic-inorganic perovskite solar cells using ultrathin Al₂O₃ layers prepared by atomic layer deposition. *Journal of Materials Chemistry A*, *3*(10), 5360-5367.

e Asl, S. D., Zarenezhad, H., Askari, M., Halali, M., & Sadrnezhad, S. K. (2020). Efficient light harvesting in perovskite layer via three-dimensional TiO₂ nanobranched nanorod scaffold. *Nano Express*, *1*(3), 030017.

Fu, F., Feurer, T., Jager, T., Avancini, E., Bissig, B., Yoon, S., Buecheler, S., & Tiwari, A. N. (2015). Low-temperature-processed efficient semi-transparent planar perovskite solar cells for bifacial and tandem applications. *Nat Commun*, *6*, 8932. <https://doi.org/10.1038/ncomms9932>

Giordano, F., Abate, A., Correa Baena, J. P., Saliba, M., Matsui, T., Im, S. H., Zakeeruddin, S. M., Nazeeruddin, M. K., Hagfeldt, A., & Grätzel, M. (2016). Enhanced electronic properties in mesoporous TiO₂ via lithium doping for high-efficiency perovskite solar cells. *Nat Commun*, *7*, 10379. <https://doi.org/10.1038/ncomms10379>

Guo, Q., Wu, J., Yang, Y., Liu, X., Sun, W., Wei, Y., Lan, Z., Lin, J., Huang, M., & Chen, H. (2020). Low-temperature processed rare-earth doped brookite TiO₂ scaffold for UV stable, hysteresis-free and high-performance perovskite solar cells. *Nano Energy*, *77*, 105183.

- Hwang, S. H., Roh, J., Lee, J., Ryu, J., Yun, J., & Jang, J. (2014). Size-controlled SiO₂ nanoparticles as scaffold layers in thin-film perovskite solar cells. *Journal of Materials Chemistry A*, 2(39), 16429-16433.
- Im, J.-H., Lee, C.-R., Lee, J.-W., Park, S.-W., & Park, N.-G. (2011). 6.5% efficient perovskite quantum-dot-sensitized solar cell. *Nanoscale*, 3(10), 4088-4093.
- Inami, E., Ishigaki, T., & Ogata, H. (2019). Sol-gel processed niobium oxide thin-film for a scaffold layer in perovskite solar cells. *Thin Solid Films*, 674, 7-11.
- Jeon, N. J., Noh, J. H., Kim, Y. C., Yang, W. S., Ryu, S., & Seok, S. I. (2014). Solvent engineering for high-performance inorganic-organic hybrid perovskite solar cells. *Nat Mater*, 13(9), 897-903. <https://doi.org/10.1038/nmat4014>
- Ke, W., Fang, G., Liu, Q., Xiong, L., Qin, P., Tao, H., Wang, J., Lei, H., Li, B., & Wan, J. (2015). Low-temperature solution-processed tin oxide as an alternative electron transporting layer for efficient perovskite solar cells. *Journal of the American Chemical Society*, 137(21), 6730-6733.
- Kim, H.-S., Lee, C.-R., Im, J.-H., Lee, K.-B., Moehl, T., Marchioro, A., Moon, S.-J., Humphry-Baker, R., Yum, J.-H., & Moser, J. E. (2012). Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. *Scientific reports*, 2(1), 1-7.
- Kim, T., Lim, J., & Song, S. (2020). Recent Progress and Challenges of Electron Transport Layers in Organic-Inorganic Perovskite Solar Cells. *Energies*, 13(21). <https://doi.org/10.3390/en13215572>
- Kojima, A., Teshima, K., Miyasaka, T., & Shirai, Y. (2006). Novel photoelectrochemical cell with mesoscopic electrodes sensitized by lead-halide compounds (2). ECS Meeting Abstracts,
- Kojima, A., Teshima, K., Shirai, Y., & Miyasaka, T. (2009). Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society*, 131(17), 6050-6051.
- Lachore, W. L., Andoshe, D. M., Mekonnen, M. A., & Hone, F. G. (2021). Recent progress in electron transport bilayer for efficient and low-cost perovskite solar cells: a review. *Journal of Solid State Electrochemistry*, 1-17.
- Lachore, W. L., Andoshe, D. M., Mekonnen, M. A., & Hone, F. G. (2022). Recent progress in electron transport bilayer for efficient and low-cost perovskite solar cells: a review. *Journal of Solid State Electrochemistry*, 1-17.
- Lee, M. M., Teuscher, J., Miyasaka, T., Murakami, T. N., & Snaith, H. J. (2012). Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. *science*, 338(6107), 643-647.
- Li, Y., Zhu, J., Huang, Y., Liu, F., Lv, M., Chen, S., Hu, L., Tang, J., Yao, J., & Dai, S. (2015). Mesoporous SnO₂nanoparticle films as electron-transporting material in perovskite solar cells. *RSC Advances*, 5(36), 28424-28429. <https://doi.org/10.1039/c5ra01540e>
- Liu, D., & Kelly, T. L. (2013). Perovskite solar cells with a planar heterojunction structure prepared using room-temperature solution processing techniques. *Nature Photonics*, 8(2), 133-138. <https://doi.org/10.1038/nphoton.2013.342>
- Liu, M., Johnston, M. B., & Snaith, H. J. (2013). Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature*, 501(7467), 395-398.
- Liu, X., Zhao, W., Cui, H., Wang, Y., Xu, T., & Huang, F. (2015). Organic-inorganic halide perovskite based solar cells-revolutionary progress in photovoltaics. *Inorganic Chemistry Frontiers*, 2(4), 315-335.
- Lu, H., Ma, Y., Gu, B., Tian, W., & Li, L. (2015). Identifying the optimum thickness of electron transport layers for highly efficient perovskite planar solar cells. *Journal of Materials Chemistry A*, 3(32), 16445-16452.
- Mahmood, K., Khalid, A., Nawaz, F., & Mehran, M. T. (2018). Low-temperature electrospray-processed SnO₂ nanosheets as an electron transporting layer for stable and high-efficiency perovskite solar cells. *J Colloid Interface Sci*, 532, 387-394. <https://doi.org/10.1016/j.jcis.2018.08.009>
- Niu, G., Guo, X., & Wang, L. (2015). Review of recent progress in chemical stability of perovskite solar cells. *Journal of Materials Chemistry A*, 3(17), 8970-8980.
- Niu, G., Li, W., Meng, F., Wang, L., Dong, H., & Qiu, Y. (2013). Study on the stability of CH₃NH₃PbI₃ films and the effect of post-modification by aluminum oxide in all-solid-state hybrid solar cells.
- Pan, H., Zhao, X., Gong, X., Li, H., Ladi, N. H., Zhang, X. L., Huang, W., Ahmad, S., Ding, L., & Shen, Y. (2020). Advances in design engineering and merits of electron transporting layers in perovskite solar cells. *Materials Horizons*, 7(9), 2276-2291.

- Pham, H. D., Yang, T. C. J., Jain, S. M., Wilson, G. J., & Sonar, P. (2020). Development of dopant-free organic hole transporting materials for perovskite solar cells. *Advanced Energy Materials*, 10(13), 1903326.
- Qiang, Y., Xie, Y., Qi, Y., Wei, P., Shi, H., Geng, C., & Liu, H. (2020). Enhanced performance of carbon-based perovskite solar cells with a Li⁺-doped SnO₂ electron transport layer and Al₂O₃ scaffold layer. *Solar Energy*, 201, 523-529.
- Qin, P., Paulose, M., Dar, M. I., Moehl, T., Arora, N., Gao, P., Varghese, O. K., Gratzel, M., & Nazeeruddin, M. K. (2015). Stable and Efficient Perovskite Solar Cells Based on Titania Nanotube Arrays. *Small*, 11(41), 5533-5539. <https://doi.org/10.1002/sml.201501460>
- Salado, M., Oliva-Ramirez, M., Kazim, S., González-Eliphe, A. R., & Ahmad, S. (2017). 1-dimensional TiO₂ nano-forests as photoanodes for efficient and stable perovskite solar cells fabrication. *Nano Energy*, 35, 215-222. <https://doi.org/10.1016/j.nanoen.2017.03.034>
- Song, T.-B., Chen, Q., Zhou, H., Jiang, C., Wang, H.-H., Yang, Y., Liu, Y., You, J., & Yang, Y. (2015). Perovskite solar cells: film formation and properties. *Journal of Materials Chemistry A*, 3(17), 9032-9050. <https://doi.org/10.1039/c4ta05246c>
- Sun, W., Choy, K.-L., & Wang, M. (2019). The role of thickness control and interface modification in assembling efficient planar perovskite solar cells. *Molecules*, 24(19), 3466.
- Sun, W., Choy, K. L., & Wang, M. (2019). The Role of Thickness Control and Interface Modification in Assembling Efficient Planar Perovskite Solar Cells. *Molecules*, 24(19). <https://doi.org/10.3390/molecules24193466>
- Tang, G., You, P., Tai, Q., Yang, A., Cao, J., Zheng, F., Zhou, Z., Zhao, J., Chan, P. K. L., & Yan, F. (2019). Solution-phase epitaxial growth of perovskite films on 2D material flakes for high-performance solar cells. *Advanced Materials*, 31(24), 1807689.
- Tomulescu, A. G., Stancu, V., Beşleagă, C., Enculescu, M., Nemneş, G. A., Florea, M., Dumitru, V., Pintilie, L., Pintilie, I., & Leonat, L. (2020). Reticulated Mesoporous TiO₂ Scaffold, Fabricated by Spray Coating, for Large-Area Perovskite Solar Cells. *Energy Technology*, 8(1), 1900922.
- Wang, S. (2018). *Function of Hole Transport Layer Components in Perovskite Solar Cells*. University of California, San Diego.
- Xiong, Y., Zhu, X., Mei, A., Qin, F., Liu, S., Zhang, S., Jiang, Y., Zhou, Y., & Han, H. (2018). Bifunctional Al₂O₃ Interlayer Leads to Enhanced Open-Circuit Voltage for Hole-Conductor-Free Carbon-Based Perovskite Solar Cells. *Solar RRL*, 2(5), 1800002.
- Yang, G., Tao, H., Qin, P., Ke, W., & Fang, G. (2016). Recent progress in electron transport layers for efficient perovskite solar cells. *Journal of Materials Chemistry A*, 4(11), 3970-3990. <https://doi.org/10.1039/c5ta09011c>
- You, J., Meng, L., Song, T.-B., Guo, T.-F., Yang, Y. M., Chang, W.-H., Hong, Z., Chen, H., Zhou, H., & Chen, Q. (2016). Improved air stability of perovskite solar cells via solution-processed metal oxide transport layers. *Nature nanotechnology*, 11(1), 75-81.
- Yu, C., Zhang, B., Chen, C., Wang, J., Zhang, J., Chen, P., Li, C., & Duan, Y. (2022). Stable and highly efficient perovskite solar cells: Doping hydrophobic fluoride into hole transport material PTAA. *Nano Research*, 15(5), 4431-4438. <https://doi.org/10.1007/s12274-021-4056-x>
- Yu, M., Guo, Y., Yuan, S., Zhao, J.-S., Qin, Y., & Ai, X.-C. (2020). The influence of the electron transport layer on charge dynamics and trap-state properties in planar perovskite solar cells. *RSC advances*, 10(21), 12347-12353.
- Zhang, B., Zhang, B., Wang, S., Yao, S., Bala, H., Sun, G., Cao, J., & Zhang, Z. (2020). Applying neoteric MgTiO₃-coated TiO₂ nanoparticulate films as scaffold layers in perovskite solar cells based on carbon counter electrode for retarding charge recombination. *Electrochimica Acta*, 338, 135884.
- Zhang, D., Cui, B. B., Zhou, C., Li, L., Chen, Y., Zhou, N., Xu, Z., Li, Y., Zhou, H., & Chen, Q. (2017). Reduction of intrinsic defects in hybrid perovskite films via precursor purification. *Chem Commun (Camb)*, 53(76), 10548-10551. <https://doi.org/10.1039/c7cc05590k>
- Zheng, X., Hou, Y., Bao, C., Yin, J., Yuan, F., Huang, Z., Song, K., Liu, J., Troughton, J., & Gasparini, N. (2020). Managing grains and interfaces via ligand anchoring enables 22.3%-efficiency inverted perovskite solar cells. *Nature Energy*, 5(2), 131-140.