ZULFAQAR Journal of Defence Science, Engineering & Technology
e-ISSN: 2773-5281
Vol. 7, Issue 1 (2024)
DOI: https://doi.org/10.58247/jdset-2023-XXXX-XX
Journal homepage: https://zulfaqarjdset.upnm.edu.my

A MINI REVIEW ON ELECTRON TRANSPORT LAYERS (ETLS) FOR PEROVSKITE SOLAR CELLS

Asyraf Hakimi Azmi[a*], Nor Azlian Abdul-Manaf[b]

[a, b] Department of Physics, Centre for Defence Foundation Studies, National Defence University of Malaysia, Sg. Besi Camp, 57000 Kuala Lumpur, Malaysia

ARTICLE INFO

ARTICLE HISTORY
Received: 30-01-2024
Revised: 23-03-2024
Accepted: 30-03-2024
Published: 30-06-2024

KEYWORDS
TiO_2 thin film
Electron transport layer
Perovskite solar cells

ABSTRACT

Perovskite solar cells (PSCs) have demonstrated rapid efficiency and advanced photovoltaic technology in the last decade. Ideally, the absorber layer in PSCs is sandwiched between a highly conductive electron transport layer (ETL) and a highly stable hole transport layer (HTL). The presence of these two layers significantly impacts the performance of PSCs. This paper will review the common materials used for ETL, various deposition techniques to grow ETL, their advantages and disadvantages, and recent advances of TiO2 films as an ETL including their challenges and future perspective. In this context, TiO2 nanostructure due to their low cost, non-toxicity, and ease of manufacture, are the most prominent photocatalyst choices. Finally, this review shows how doped TiO2 can be a beneficial approach to improve the PSC's performance and stability.

1.0 ROLE OF ETL IN PSCs

Solar energy is the energy obtained by capturing heat and light from the Sun. The sun is also considered as an infinite energy source and can be accessed nearly everywhere, making it the most reliable energy source. Electrical devices that convert light energy or photon from the sun to electrical energy through photovoltaic (PV) effect are called solar cells. The first generations of solar cells were based on crystallite silicon but, it required very complex fabrication process and high cost. The second generation of solar cells is based on thin films. Typical materials used for this kind of solar cell are cadmium telluride (CdTe) and copper-indium-galium-diselenide (CIGS). The photovoltaic technologies for third generation are based on more recent chemical compounds and includes several thin-film technologies often described as emerging photovoltaics. In addition, technologies using nanocrystalline films based on new materials and cutting-edge technologies. Perovskite solar cells (PSCs) is one kind of the third generation of solar cells that consists of perovskite structure compound as an active layer with speedy increasing in power conversion efficiency (PCE) from 13% to certified 26% during the past 10 years [1-3]. Perovskite has an absorption coefficient ($\sim$106 cm^{-1}) that is significantly higher than crystalline silicon. The conventional device structure of PSCs consisted of transparent conducting electrode (TCO) layer of fluorine-doped tin oxide (FTO) as bottom electrode, an electron transport layer (ETL), perovskite absorption layer, a hole-transport layer (HTL) and top electrode as shown in Figure 1. There are two types of PSCs device architecture according to the arrangement of the precedent ETL or HTL that attributed to the regular n-type – intrinsic – p-type (n-i-p) structure or inverted p-type – intrinsic – n-type (p-i-n) structure, respectively depend on which transport material on the exterior portion of perovskite will encounter light first. Figure 1 shows n-i-p and p-i-n device structure. In n-i-p structure, the ETL is deposited first, followed by perovskite active layer and HTL so that ETL encounters sunlight first. In p-i-n structure, the HTL is deposited first followed by perovskite active layer and ETL, where in this case, the light falls on the HTL first.

*Corresponding Author | Abdul Manaf, N. A. | azlian@upnm.edu.my

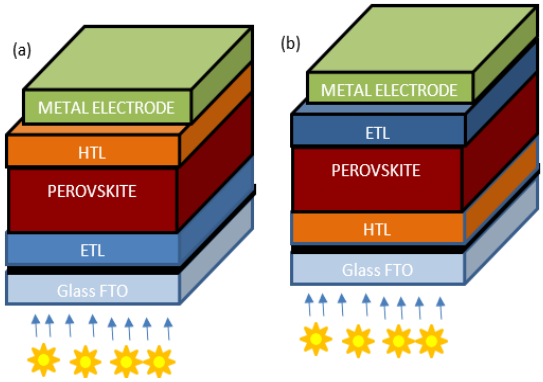

Figure 1. (a) n-i-p and (b) p-i-n devices structure

ETL plays a crucial role in extracting and transporting photogenerated electron carriers and serves as a hole-blocking layer by suppressing charge recombination as one of the most important components for photovoltaic devices [4]. The physical properties of the ETL, including charge mobility, energy level alignment, defective states, morphology, and related interfacial properties, are significant for the photovoltaic performance [5]. To achieve a high-performance PSCs, the presence of an ETL is required to meet the following criteria. Firstly, the ETL must have good energy-level alignment, so the charge transfer and hole blocking can be efficient. Next, have the high electron mobility to enable fast electron transport within the ETL. Besides that, ETL materials must have a wide band gap to ensure high transparency and allow lighter to pass through it so that light absorption by the perovskite materials can be maximized. Other than that, materials must have compatible energy levels, where the ETL must have a compatible conduction band minimum and valence band maximum in relation to the energy levels of the perovskite light harvester to facilitate electron transfer and block hole transport from the perovskite layer. Lastly, easy processing deposition techniques such as solution processed, is to ensure uniform and high-quality film formation and enable mass production [6]. Even though various groups claimed to have a PCE of more than 13% for perovskite devices without the ETL [7-8], the formation of ETL in PSCs is still dominant in terms of efficiency and stability of the devices. Juarez-Perez et al. compared the device performance of the complete PSCs with the ETL-free device, they observed that the absence of ETL had a significant impact on the electrical output parameter and device efficiency [9].

By removing the TiO_2 layer compact, it has little effect on the open circuit potential, V_{oc}, but affects deleteriously the short circuit photocurrent, J_{sc}, and the fill factor, *FF*, nearly having the photoconversion efficiency, η, in comparison to the complete device. Zhang et al. also reported a reduction of efficiency from 14.2% to 2.7% upon the removal of the ETL [10]. They observe that the ETL free planar cells have almost zero stabilized power output and there is a short-lived effect responsible for hysteresis in these devices, which then disappears during the stabilized power scan. It was also reported that the PCE of the ETL free device could reach up to 14.1%, but the complete cells exhibited superior efficiency of 16.1% [8]. The efficiency improvement was due to the enhancements of *FF* and J_{SC}. The chlorine may passivate the FTO/perovskite interface, and the passivation seems to be effective with the presence of TiO_2 as ETL.

2.0 ORGANIC AND INORGANIC MATERIALS FOR ETL

Organic material such as fullerene (C60), graphene and its derivative have been widely used as ETL in PSCs [12-13]. The advantages of organic ETLs is that they can be easily prepared by solution process and the devices showed good performance, but their environmental, thermal, and photostability is quite concerning for the device's long-term stability. Fullerene-based molecules, is an organic material that could minimize the density of defects at the perovskite/ETL interface. Pandey et al. had successfully deposited a thin layer of C60 using spin coating and observed that C60 has bandgap around 1.7 eV [13]. Ke et al. reported that insertion of C60 as an ETL, produced by vacuum process with thickness of 7.5 nm could enhance the short circuit current density (J_{SC}) and fill factor (*FF*) values of PSCs to the maximum, leading to a PCE of 15.1% [8]. Furthermore, the employment of C60 as an ETL helped to avoid trapped charge induced degradation in the presence of moisture. Study from Yoon et al. using a room temperature vacuum-processed C60 as an ETL has demonstrated a PCE of 19.1% [14]. The highly homogeneous, uniform, and dense ETL with a thickness of 35 nm was found to not only passivate the grain boundaries and surfaces of the perovskite layer, but also enhanced the charge transport property. The results of the

*Corresponding Author | Abdul Manaf, N. A. | azlian@upnm.edu.my

structure of conventional of (Methyl-ammonium lead iodide) MAPI PSCs with C60 as ETL is represented in Figure 2.

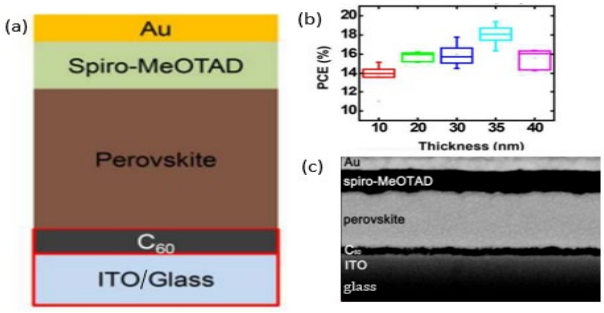

Figure 2. (a) The structures of conventional perovskite solar cells with C60 layer as ETL, (b) PCE comparison with different C60 thickness and (c) cross sectional FESEM image of a flexible MAPbI3 perovskite solar cell

Other organic materials that have been reported as ETL are graphene and reduced graphene. To improve the PSCs electron efficiency, graphene and reduced graphene oxide, are typically doped with other inorganic materials to create nanocomposite ETLs. Biccari et al. investigated the effects of different graphene-based ETLs in sensitized MAPI photoelectrodes [12]. They observed that graphene based ETLs significantly improve both the carriers collection and the crystalline quality of the active material. The FESEM image in Figure 3 also demonstrated the enhancement of crystal size and shape regularity after the addition of graphene. From this work, the PSCs produced by graphene-doped TiO_2, showed an improvement in PCE with 16% efficiency compared to undoped TiO_2 (14.6% PCE). Futher work by Agresti et al. proposed a new PSCs structure by including lithium neutralized graphene oxide (GO-Li) as the ETL on top of the mesoporous TiO_2 substrate and this result showed an improvement of short circuit current and fill factor [15]. The main effect of GO-Li is its improving the electron injection from the sensitizer to the m-TiO_2 layer by remarkably increasing the J_{SC} and demonstrated an impressive PCE of 12% over the performance of the reference sample (9.6%). Study done by Chandrasekhar et al. has been reported in 2017 using Zinc Oxide (ZnO) and doped ZnO with different concentration of graphene as ETL [16]. Although, the SEM images show the similar morphology between pristine ZnO and graphene doped ZnO, but the PCE of PSCs increased from 7.01% (ZnO ETL) to 10.34% (graphene doped ZnO ETL). This study also showed an improvement of PV performance with 75% increasing of photon-to-current conversion efficiency after using graphene doped ZnO as an ETL layer in PSCs. In 2020, Chandrasekhar et al. also demonstrated the photovoltaic performance of PSCs by employing nitrogen-doped graphene (NG)/ZnO as an ETL [17]. This study varying the NG concentration from 0 to 1 wt% with an increment of 0.2 wt% in ZnO. The pristine ZnO are used as reference device. PCE are improved by increasing the concentration of NG from 0 wt% to 0.8 wt% and then decreased with 1.0 wt% of NG. PCE from 12.87% to 16.82% and exhibited a hysteresis free photovoltaic behaviour in comparison to pristine ZnO. Ahmed et al. prepare PSCs device with ZnO/graphene quantum dots (GQDs) used as an ETL in order to inspected the role of the ZnO/GQD ETL, they compare the different volume ratios of GQDs with 0.0%, 0.5%, 1.0%, 1.5%, 2.0%, and 2.5% and the 0% volume of GQD is marked as reference device [18]. As the result, all PV parameters were enhanced, together with an increment of the PCE from 10 % to 17.67%.

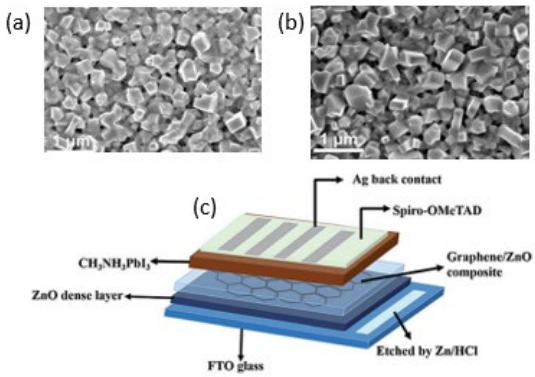

Figure 3. (a) SEM image of the pristine TiO_2, (b) graphene-doped TiO_2 [12], (c) structure for grapheme doped ZnO as an ETL in PSCs [16]

*Corresponding Author | Abdul Manaf, N. A. | azlian@upnm.edu.my

In 2018, Zhu et al. investigate the effect of the graphene in the tin oxide (SnO_2) as an ETL on the photovoltaic performance [19]. The incorporation of graphene in the SnO_2, improved the *Jsc, FF*, open circuit voltage (Voc), and PCE. The enhancement are mainly attributed to the improved the electron extraction in the ETL layer and the efficient charge separation at the perovskite/ETL interfaces. The PCE increase from 17.01% to 18.11% with increase of graphene dopant. Besides that, Hong et al. have been improved efficiency in 2020 of PSCs by doping 5% of volume nitrogen-doped graphene oxide (NGO) in SnO_2 as an ETL [20]. The NGO acts as an oxidizing agent for SnO_2. Based on the photovoltaic parameters, the greatest PCE was obtained at 16.54% with the doping of NGO compared with undoped SnO_2 with 15.36% of PCE. It is believed that the PCE of the PSCs with NGO in the SnO_2 layer were significantly higher due to the reduction of the trap states in the SnO_2: NGO composite layer.

Many inorganic materials can be considered to be used as ETL including titanium dioxide (TiO_2), zinc oxide (ZnO), cadmium sulfide (CdS) and cadmium selenide (CdSe), and tin oxide (SnO_2). ZnO has a band gap similar to TiO_2 of 3.2 eV. The electron mobility of ZnO is 200 $cm^2V^{-1}s^{-1}$, which is two orders of magnitude higher than that of TiO_2 [21]. Thus, it is expected that the used of ZnO-based as ETL in a PSCs could enhance the electron extraction and transport in the PSCs device. There are many synthesize methods and deposition techniques reported of ZnO thin films. Deghan et al.[22] studied and compared several deposition techniques of ZnO through spin coating, spray pyrolysis and SILAR, and observed their performance as ETL in PSCs. They reported the ETL grown using spin coating technique demonstrated good performance compared to spray pyrolysis and SILAR technique since it produced the lowest bandgap of 3.27 eV and highest PCE of 7.0%. Spin coating method has more advantages such as efficiency, low cost, and ease of production. Other method was studied by Zhao et al. using solution processed and sputtered method [23]. The sputtered ZnO layer exhibited larger grain size, higher energy-level, better optical transmission and higher conductivity compared to solution processed technique. The device with the sputtered ETL had an excellent performance due to the improvement in the V_{OC} and *FF*. The increase in V_{oc} was probably due to the lower recombination rate and the larger surface area at the interface that contributed to an intense improvement in the thermochemical stability.

On the other hand, several sulfides and selenides material were also considered as inorganic material for ETL in PSCs. Uniform metal chalcogenide (MCs) film was deposited using a low-cost and scalable chemical bath deposition (CBD) method and achieve near 11% PCE [24]. They discovered that the annealing temperature process had no effect in improvement of devices efficiency. They concluded that metal chalcogenide can be a good ETL since it showed high stability, reproducibility and a better scalability for low temperature deposition, which this can be extended to be applied in flexible substrates. In addition, researcher from China introduced low-temperature processed PSCs using metal sulfide as electron transport layer [25]. In order to find the effect of metal sulfide on device performance, perovskite solar cells with and without electron transport layer were fabricated. Only 3.58% PCE achieved for the ETL free device. This study varying the different thickness of the metal sulfide layer with 30 nm, 50 nm and 100 nm. The layer of 30 nm was fabricated, a *Voc* of 1.05 V, a *Jsc* of 16.14 mA/cm^2 and a *FF* of 0.66 were achieved, resulting in the champion PCE of 11.17%. From the photovoltaic performance reveal the presence of metal sulfide layer results in efficient collection and reduced recombination.

Recently, SnO_2 has received significant attention as an ETL for PSCs, and it is regarded as the most promising as TiO_2. Several groups reported that SnO_2 displayed a band gap of 3.8 eV, and the electron mobility of 250 $cm^2V^{-1}s^{-1}$, which both is higher than that of the TiO_2 or ZnO counterparts [21]. Faster electron mobility might improve the ETL's capacity for transporting electrons, while a wider band gap might prevent the ETL from absorbing photons with high energy, which might result in little current loss. In addition, SnO_2 nanoparticles have the advantages of possessing good anti-reflective properties and thermal stability [26]. Ren et al. studied the solution processed of pristine SnO_2 and Niobium (Nb) doped SnO_2 [27]. The result showed that the power conversion efficiency of PSCs based on SnO_2 doped Nb ETL was raised to 17.57% from 15.13% (pristine SnO_2). SnO_2 doped Nb ETL show an improved surface morphology, higher electron mobility, larger electrical conductivity, and enhanced electron extraction. Besides that, the method of deposition of SnO_2 also become one of the effect of device efficiency. PCEs estimated from the stable photocurrent are only 4.5% (sol–gel SnO_2) and 8.7% (hydrothermal SnO_2), respectively [28]. They also observed the increment of PCE of the PSCs to 18.8% after adding C60 to SnO_2 ETL. On the other hand, the UV/ozone (UVO) pre-treatment can increased the PCE of the device. A study show new method is the regrowth of the new SnO_2 nanocrystallines absorbed on the FTO or ITO surfaces introduced by UVO pretreatment [29]. PSCs devices based on their new SnO_2 ETL show high PCEs up to 20.5%, with a steady-state output of 20.1%.

*Corresponding Author | Abdul Manaf, N. A. | azlian@upnm.edu.my

2.1 Brief History Of TiO_2

TiO_2 is a well-known inorganic material that is commonly used as buffer layer in sensors and ETL in solar cells. TiO_2 nanoparticle has a bandgap of 3.0 to 3.2 eV and an electron mobility of approximately 1 $cm^2V^{-1}s^{-1}$ [21]. There are numerous production methods available to create a good TiO_2 layer with the necessary parameter. TiO_2 has high electrical conductivity even before it is transformed into nanocrystallites. As a result, TiO_2 requires a high temperature process. TiO_2 compact layer is usually constructed on FTO substrate, which can withstand high temperatures of up to 700°C [30]. TiO_2 contains various phases, the most notable are anatase and rutile [31]. A three-dimensional (3D) crystal structure of anatase and rutile are shown in Figure 4. Both TiO_2 phases have tetragonal unit cell and crystal structures composed of TiO_6 octahedra. Anatase and rutile TiO_2 have band gaps of about 3.20 eV and 3.03 eV, respectively [32]. TiO_2 -based nanostructures have been intensively studied in research and deployed in a range of applications over the last few decades. When a photon (with energy equal to or greater than the TiO_2 bandgap) impinges TiO_2 particles or film, electrons are triggered from the valance band to the conduction band, resulting in electron-hole pairs. The formed charge carriers migrate towards the surface and react with the adsorbed chemicals, thereby degrading the organic pollutants. The process shown in Figure 5.

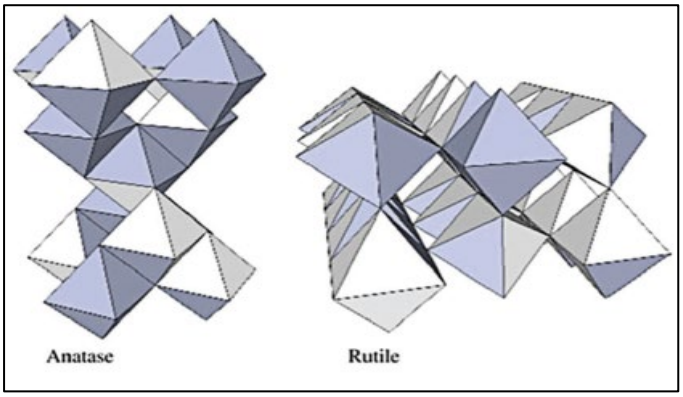

Figure 4. The three-dimensional representation of the crystal structure of anatase and rutile of TiO_2 [41]

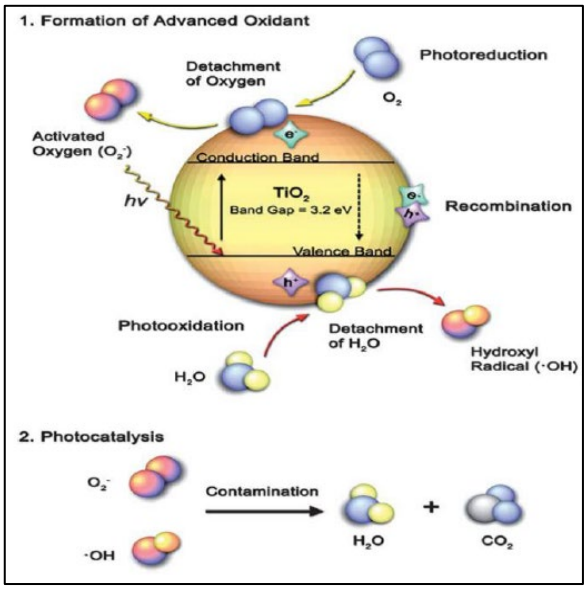

Figure 5. Photocatalysis process of TiO_2 [42]

3.0 TiO_2 AS THIN FILMS

TiO_2-based photocatalytic thin films and nanostructures commonly employed in a wide range of applications such as remediation, self-cleaning windows, water splitting, hydrogen release, and antibacterial material due to their interesting chemical, electrical, and optical properties [33-35]. TiO_2 thin

*Corresponding Author | Abdul Manaf, N. A. | azlian@upnm.edu.my

films can be applied to various type of substrates, and instead of bulk materials, TiO_2 thin films are used to aims for significant cost savings. In addition, the thin film catalysts can reduce the recombination of UV-activated electrons and holes, thereby increasing the quantum efficiency [36-37]. TiO_2 thin films at the nanoscale, enables distinct mechanical, chemical, and physical surface functions, such as increased surface area and improved photocatalytic activity [38]. TiO_2 in thin film also exhibit high stability in aqueous solutions, no photocorrosion under bandgap illumination, as well as exceptional surface properties [39]. Another important characteristic of TiO_2 films related to photo-generation of electron hole pairs is that it can improve the surface with photo-induced hydrophilicity [40].

3.1 Deposition Techniques For TiO_2 Thin Film

TiO_2 thin films have been synthesized by several sophisticated techniques such as chemical vapor deposition (CVD) [38,50], metal organic chemical vapour deposition (MOCVD) [38,43], hydrothermal synthesis [44,55], sputtering [38,45], liquid phase deposition (LPD) [38,46], electrophoretic deposition [38,47], sol-gel [38,57-61,64,66], atomic layer deposition (ALD) [38,48], doctor-blade [38,53,54], etc. The synthesis methods and processing conditions have significant impact on the physical properties of the materials. Since the microstructure and physical properties of TiO_2 affect its photocatalytic activity, the proper choice of deposition technique is important for a good results. Table 1 shows the summary of TiO_2 properties thin film deposited by various technique.

Table 1: Common methods for TiO_2 coating and their advantages and disadvantages

Method	Description	Advantages	Disadvantages	References
Sputtering	Use the energy of a plasma (partially ionized gas) on the surface of a target (cathode), to pull the atoms of the desired material one by one and deposit them on the substrate (Pressure of 0.8 Pa)	• Suitable for insulator and semiconductor substrate • Good film adhesion	• Risk of substrate damage due to ionic bombardment • Relatively low coating rates	[38, 45, 49]
CVD	A thin film is formed on a heated substrate from a gaseous phase in a closed chamber at a relatively higher temperature The process which vapour phase materials are condensed to produce solid phase material	• Thickness of the layer can be controlled • Produce uniform films at low or high rate • Compatibility with good adhesion	• High temperature • High cost • High reaction temperature • Low deposition rate • Presence of corrosive gases	[38, 44, 50-51]
Sol-gel	The process is called wet chemical method for the synthesis of various nanostructures. In this method, the molecular precursor is dissolved in water or alcohol and converted to gel by heating, stirring and hydrolysis /alcoholysis until the solution become sol-gel phase	• Simple and easy • Low cost • Reliability and reproducibility • Suitable for any type of substrate • Full coating on substrate • low processing temperature	• Required long processing time • Not suitable for thick layer • Notable to control and measure thickness during deposition	[38, 44, 57-61, 64, 66]

*Corresponding Author | Abdul Manaf, N. A. | azlian@upnm.edu.my

Method	Description	Advantages	Disadvantages	References
Doctor-blade	The slurry is poured on a substrate, and a blade applies unidirectional shear force to the substrate	• Simplest, easy control of film thickness • Suitable for mass production • Low cost	• Slow evaporation • Not suitable for low thickness	[38, 53-54]
Hydro-thermal	Comprises a variety of methods for crystallizing substances from high-temperature aqueous solutions at high vapour pressures	• Simple operation technique • Ability to grow large, high-quality crystals	• High cost • Required high temperature • It is impossible observing the crystal grow	[38, 44-55]

3.2 TiO_2 Grown Using Sol-Gel Method

The sol-gel process has become a popular method for preparing TiO_2 films due to its facile and matured application. The sol-gel method also has become one of the most popular approaches due to its effectiveness, homogeneity and dependability [38]. The sol-gel coating can be done at room temperature without the use of any expensive equipment [38]. The hydrolysis and polycondensation processes of the precursors, which are mainly metal organic compounds or inorganic metal salts, result in a colloidal suspension (a solution). Following polymerization and subsequent solvent loss, the liquid transforms into a solid gel phase. The sol-gel route combined with spin coating has been widely applied to coat metallic film in different substrates such as glass, silicon wafer, polyethylene terephthalate (PET), ceramic, and crystal substrate. By controlling the sol-to-gel transition and thereby the sol viscosity, a variety of shapes with desired porosity and texture can be obtained [56]. Sol-gel method allows to control over the porosity, texture, and chemical composition of deposited materials. However, in order to prepare films with controlled crystal size and texture, optimum conditions should be maintained for controlling the precursor reactivity [38].

You et al. employed a low temperature solution processes TiO_2 for ETL on two type of substrates a glass substrate known as rigid cell and flexible polymer substrate (PET) named as flexible cell [57]. The solution was spin coated on both of the substrates at 3000 rpm for 30 s and heat treated on a hot plate at 100°C for 30 min. The heat-treatment ensures the following orthogonal processability of perovskite solution. The rigid cell exhibited 18.2 % PCE under sun condition of AM1.5 G 100 mW/cm^2 and the flexible cell has 15.8% PCE. Furthermore, the flexible perovskite solar cells exhibited good mechanical stability against repeated bending, so it maintained ~95% of its initial PCE after 1000 repeated bending cycles. Khan et al. studied the structural, electrical and optical properties of multilayer TiO_2 thin films deposited by sol-gel spin coating [58]. They presented the comparisons among the stacked layers of TiO_2 thin films. After homogenous solution of TiO_2 is prepared, it was spin coated at 2400 rpm for 30 second per layer. The experiment was repeated for the multilayer of the films. As the results, XRD confirms the anatase phase of TiO_2. The resistivity decreased with the increasing number of layer. Optical properties of the film showed high transmittance in the visible region and the optical band gap decreased by increasing the layers due to the formation of sub valence band in the forbidden band of TiO_2. El Haimeur et al. synthesized TiO_2 using sol-gel process using butanol as solvent and acetic acid as catalyst [59]. They studied the effect of thickness on the morphological, structural and optical properties was investigated, as well as their applicability as electron transporting layer for planar PSCs. The distribution histograms of the grain sizes show a relatively narrow peak for all thicknesses, indicating that the films are morphologically uniform. XRD confirms the anatase phase of TiO_2 which grows mainly along (1 0 1) direction. Regardless of thicknesses, all films have a similar peak shape in the absorbance spectra graph. The results showed an improvement in charge transport and electron extraction behavior using the 50 nm TiO_2 layer, and thus a rise in the devices power conversion efficiency with 13.8% PCE.

3.3 TiO_2 Thin Film

In this section, only pristine TiO_2 without any material doping used as an ETL for PSCs devices. Tahir et al. has been synthesized TiO_2 using sol-gel and spin coating on the glass substrate [60]. In order to prepare

*Corresponding Author | Abdul Manaf, N. A. | azlian@upnm.edu.my

the solution, 50 mL ethanol was stirred for 15 minutes in 5 mL of acetic acid, the 6.3 mL of titanium tetraisopropoxide (TTIP) add drop by drop and continuous stirring for another 15 minutes. The transparent sol solution was aged for 24 hours. Next, the sol-gel was spin coating with speed of 3000 rpm and spin time 15 seconds. As the result Tahir et al. concluded that sol-gel coating technique employed excellent result better than any other techniques [60]. The thin films are uniform, crack free and good coverage of glass substrate with a spherical shape. Sławek et al. studied the influence of thickness of compact TiO_2 as an ETL [61]. The thickness was controlled with the different spin coating speed. The result show optimal thickness for the studied was 19.5 nm, resulting in the highest PCE of 13.6%. From the results, shows that the thickness of the compact TiO_2 ETL clearly affects the performance of MAPbI3 PSCs. Futhermore, they noticed a clear gradual decrease in PCE from 13.6% to 7.3% along with the thickening of the compact TiO_2 ETL. Mandati et al. has been compared two different deposition methods of TiO_2 which are spin coating and bar coated [62]. For the bar coated technique, the precursor was dropped at the interface of bar and substrate. The wire wounded bar was then moved gradually to spread the precursor solution followed by drying the wet film in the air. As the result, the PSCs grown on bar coated ETL have exhibited a power conversion efficiency of 12.1% while the ones on spin coated ETL showed PCE of 11.5%.

3.4 Doped TiO2 Thin Film

The doping process of TiO_2 is an essential method for overcoming the rapid recombination of photogenerated charge carriers. The doping method can reduce the rate of electron-hole pair recombination. Below are the several study of doped TiO_2 as an ETL with various material such as graphene, Zinc (Zn), Tin (Sn), and Magnesium (Mg). Dadashbeik et al. designed a simulation technique using a three-dimensional (3D) finite element method (FEM) to comparing PCE of PSCs on graphene and TiO_2 /graphene as an ETL [63]. As the result, graphene as an ETL has PCE of 16.03% but after proposed TiO_2 /graphene as an ETL, the PCE increase to 17.8%. This is due to the increased in the mobility of carriers. Ebrahimi et al. synthesized with different amount of volume of graphene quantum dots (GQD) to the mesoscopic TiO_2 using spin coating technique [64]. The results demonstrated that 2.5% volume of graphene showed the best PCE with 14.36% approximately 50% improvement compared to the un-doped PSCs has only PCE of 9.55%. This work clearly shows that doping of GQDs as a modifier to the TiO_2 layer can be a beneficial approach to improve the PSCs's performance and stability. Liu X et al. deposited Zn-doped TiO_2 as an ETL using low temperature solution processed route [65]. The different volume of Zn has been investigated. They found that Zn-doped TiO_2 films possess less trap-state density and better conductivity, compared to undoped thin films, which contributes to the promotion of short circuit current. The best PCE was 17.60% for the 4.5% volume of Zn. The outstanding performance using the Zn-doped TiO_2 ETL originates from high electrical conductivity, low trap state density, and enhanced electron extraction.

In order to enhance the planar structure of PSCs, Cai et al. using the Sn-doped TiO_2 as an ETL with low temperature fabrication procedure (below 100 ^oC) [66]. They compared with pristine TiO_2 (PCE =13.30%) and the Sn-doped TiO_2 (PCE = 15%-17%) which was almost 29.3% improvement. This result demonstrated that the Sn-doped TiO_2 is more efficient for photogenerated electron extraction and transport, showing lower trap-state density and higher conductivity. Arshsad et al. prepared Mg-doped TiO_2 as an ETL to enhance the optical and morphological properties of the layer and the interface [67]. They find that Mg doped in mesoporous TiO_2, was significantly improved thereby providing an interface for the growth of absorber layer. The best PCE was with 3 wt% Mg doped TiO_2 with PCE of 14.65%.

4.0 CONCLUSION

ETL can be an important factor in the fabrication of PSCs that guarantees the PSCs's excellent efficiency. This review cover the common materials for ETL, the list of deposition techniques of the ETL and device performance when doped TiO_2 are presented. This included the improvements to the electric structure and intrinsic properties, enhancements to electrical conductivity by boosting carrier density and mobility, and improvements to bandgap alignments, interface trap density, and distribution. Sol-gel technology has recently been used to create both pure TiO_2 films and modified or doped TiO_2 films for photocatalytic dye degradation. Although TiO_2 have several drawbacks such as its poor ability to absorb solar irradiation, its wide bandgap (3.2 eV) limits the use of visible light as the light source and the adsorption capacity of TiO_2 is relatively low. Continued research in this field is expected to lead to a better understanding and indicate a way to overcome existing limitations.

*Corresponding Author | Abdul Manaf, N. A. | azlian@upnm.edu.my

5.0 CONFLICT OF INTEREST

The authors declare no conflicts of interest.

6.0 AUTHORS CONTRIBUTION

Azmi, A. H. (Validation; Investigation; Writing - origin draft)
Abdul manaf, N. A. (Conception; Funding acquisition; Supervision)

7.0 ACKNOWLEDGEMENTS

This research is fully supported by GPJP, UPNM/2023/GPPP/SG/7. The authors fully acknowledge National Defence University Malaysia for the approved fund which makes this important research viable and effective.

REFERENCES

[1] NREL. (2021). National Renewable Energy Laboratory Best Research Cell Efficiency Chart.
[2] Correa-Baena, J. P., Saliba, M., Buonassisi, T., Grätzel, M., Abate, A., Tress, W., & Hagfeldt, A. (2017). Promises and challenges of perovskite solar cells. Science, 358(6364), 739-744.
[3] Kim, H. S., Lee, C. R., Im, J. H., Lee, K. B., Moehl, T., Marchioro, A., ... & Park, N. G. (2012). Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. Scientific reports, 2(1), 591.
[4] Zhou, H., Chen, Q., Li, G., Luo, S., Song, T. B., Duan, H. S., ... & Yang, Y. (2014). Interface engineering of highly efficient perovskite solar cells. Science, 345(6196), 542-546.
[5] 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.
[6] Pathak, S. K., Abate, A., Ruckdeschel, P., Roose, B., Gödel, K. C., Vaynzof, Y., ... & Steiner, U. (2014). Performance and stability enhancement of dye-sensitized and perovskite solar cells by Al doping of TiO2. Advanced Functional Materials, 24(38), 6046-6055.
[7] Liu, D., Yang, J., & Kelly, T. L. (2014). Compact layer free perovskite solar cells with 13.5% efficiency. Journal of the American Chemical Society, 136(49), 17116-17122.
[8] Ke, W., Fang, G., Wan, J., Tao, H., Liu, Q., Xiong, L., ... & Yan, Y. (2015). Efficient hole-blocking layer-free planar halide perovskite thin-film solar cells. Nature communications, 6(1), 6700.
[9] Juarez-Perez, E. J., Wuβler, M., Fabregat-Santiago, F., Lakus-Wollny, K., Mankel, E., Mayer, T., ... & Mora-Sero, I. (2014). Role of the selective contacts in the performance of lead halide perovskite solar cells. The journal of physical chemistry letters, 5(4), 680-685.
[10] Zhang, Y., Liu, M., Eperon, G. E., Leijtens, T. C., McMeekin, D., Saliba, M., ... & Snaith, H. J. (2015). Charge selective contacts, mobile ions and anomalous hysteresis in organic–inorganic perovskite solar cells. Materials Horizons, 2(3), 315-322.
[11] Upama, M. B., Elumalai, N. K., Mahmud, M. A., Wang, D., Haque, F., Gonçales, V. R., ... & Uddin, A. (2017). Role of fullerene electron transport layer on the morphology and optoelectronic properties of perovskite solar cells. Organic Electronics, 50, 279-289.
[12] Pescetelli, S., Agresti, A., Di Carlo, A., Bonaccorso, F., & Busby, Y. (2018, September). Graphene and Related 2D Materials: A Winning Strategy for Enhanced Efficiency and Stability in Perovskite Photovoltaics. In 2018 IEEE 4th International Forum on Research and Technology for Society and Industry (RTSI) (pp. 1-4). IEEE.
[13] Pandey, A. K., & Nunzi, J. M. (2007). Rubrene/fullerene heterostructures with a half-gap electroluminescence threshold and large photovoltage. Advanced Materials, 19(21), 3613-3617.
[14] Yoon, H., Kang, S. M., Lee, J. K., & Choi, M. (2016). Hysteresis-free low-temperature-processed planar perovskite solar cells with 19.1% efficiency. Energy & Environmental Science, 9(7), 2262-2266.
[15] Agresti, A., Pescetelli, S., Cinà, L., Konios, D., Kakavelakis, G., Kymakis, E., & Carlo, A. D. (2016). Efficiency and stability enhancement in perovskite solar cells by inserting lithium-neutralized graphene oxide as electron transporting layer. Advanced Functional Materials, 26(16), 2686-2694.
[16] Chandrasekhar, P. S., & Komarala, V. K. (2017). Graphene/ZnO nanocomposite as an electron transport layer for perovskite solar cells; the effect of graphene concentration on photovoltaic performance. Rsc Advances, 7(46), 28610-28615.

*Corresponding Author | Abdul Manaf, N. A. | azlian@upnm.edu.my

[17] Chandrasekhar, P. S., Dubey, A., & Qiao, Q. (2020). High efficiency perovskite solar cells using nitrogen-doped graphene/ZnO nanorod composite as an electron transport layer. Solar Energy, 197, 78-83.
[18] Ahmed, D. S., Mohammed, M. K., & Majeed, S. M. (2020). Green synthesis of eco-friendly graphene quantum dots for highly efficient perovskite solar cells. ACS Applied Energy Materials, 3(11), 10863-10871.
[19] Zhu, M., Liu, W., Ke, W., Xie, L., Dong, P., & Hao, F. (2018). Graphene-modified tin dioxide for efficient planar perovskite solar cells with enhanced electron extraction and reduced hysteresis. ACS applied materials & interfaces, 11(1), 666-673.
[20] Hong, J. A., Jung, E. D., Yu, J. C., Kim, D. W., Nam, Y. S., Oh, I., ... & Song, M. H. (2019). Improved efficiency of perovskite solar cells using a nitrogen-doped graphene-oxide-treated tin oxide layer. ACS applied materials & interfaces, 12(2), 2417-2423.
[21] Tiwana, P., Docampo, P., Johnston, M. B., Snaith, H. J., & Herz, L. M. (2011). Electron mobility and injection dynamics in mesoporous ZnO, SnO2, and TiO2 films used in dye-sensitized solar cells. ACS nano, 5(6), 5158-5166.
[22] Dehghan, M., & Behjat, A. (2019). Deposition of zinc oxide as an electron transport layer in planar perovskite solar cells by spray and SILAR methods comparable with spin coating. RSC advances, 9(36), 20917-20924.
[23] Zhao, W., Li, H., Li, D., Liu, Z., Wang, D., & Liu, S. F. (2019). Comprehensive investigation of sputtered and spin-coated zinc oxide electron transport layers for highly efficient and stable planar perovskite solar cells. Journal of Power Sources, 427, 223-230.
[24] Abulikemu, M., Barbé, J., El Labban, A., Eid, J., & Del Gobbo, S. (2017). Planar heterojunction perovskite solar cell based on CdS electron transport layer. Thin Solid Films, 636, 512-518.
[25] Liu, J., Gao, C., Luo, L., Ye, Q., He, X., Ouyang, L., ... & Lau, W. (2015). Low-temperature, solution processed metal sulfide as an electron transport layer for efficient planar perovskite solar cells. Journal of Materials Chemistry A, 3(22), 11750-11755.
[26] Noh, M. F. M., Soh, M. F., Teh, C. H., Lim, E. L., Yap, C. C., Ibrahim, M. A., ... & Teridi, M. A. M. (2017). Effect of temperature on the properties of SnO2 layer fabricated via AACVD and its application in photoelectrochemical cells and organic photovoltaic devices. Solar Energy, 158, 474-482.
[27] Ren, X., Yang, D., Yang, Z., Feng, J., Zhu, X., Niu, J., ... & Liu, S. F. (2017). Solution-processed Nb: SnO2 electron transport layer for efficient planar perovskite solar cells. ACS applied materials & interfaces, 9(3), 2421-2429.
[28] Zhu, Z., Bai, Y., Liu, X., Chueh, C. C., Yang, S., & Jen, A. K. Y. (2016). Enhanced efficiency and stability of inverted perovskite solar cells using highly crystalline SnO2 nanocrystals as the robust electron-transporting layer. Advanced Materials, 28(30), 6478-6484.
[29] Dong, Q., Li, J., Shi, Y., Chen, M., Ono, L. K., Zhou, K., ... & Wang, L. (2019). Improved SnO2 electron transport layers solution-deposited at near room temperature for rigid or flexible perovskite solar cells with high efficiencies. Advanced Energy Materials, 9(26), 1900834.
[30] Yang, J. K., Liang, B., Zhao, M. J., Gao, Y., Zhang, F. C., & Zhao, H. L. (2015). Reference of Temperature and Time during tempering process for non-stoichiometric FTO films. Scientific reports, 5(1), 15001.
[31] Hanaor, D. A., & Sorrell, C. C. (2011). Review of the anatase to rutile phase transformation. Journal of Materials science, 46, 855-874.
[32] Pant, B., Pant, H. R., Park, M., Liu, Y., Choi, J. W., Barakat, N. A., & Kim, H. Y. (2014). Electrospun CdS–TiO2 doped carbon nanofibers for visible-light-induced photocatalytic hydrolysis of ammonia borane. Catalysis Communications, 50, 63-68.
[33] Pant, B., Pant, H. R., Park, M., Liu, Y., Choi, J. W., Barakat, N. A., & Kim, H. Y. (2014). Electrospun CdS–TiO2 doped carbon nanofibers for visible-light-induced photocatalytic hydrolysis of ammonia borane. Catalysis Communications, 50, 63-68.
[34] Javid, A., Kumar, M., Ashraf, M., Lee, J. H., & Han, J. G. (2019). Photocatalytic antibacterial study of N-doped TiO2 thin films synthesized by ICP assisted plasma sputtering method. Physica E: Low-dimensional Systems and Nanostructures, 106, 187-193.
[35] Varnagiris, S., Medvids, A., Lelis, M., Milcius, D., & Antuzevics, A. (2019). Black carbon-doped TiO2 films: Synthesis, characterization and photocatalysis. Journal of Photochemistry and Photobiology A: Chemistry, 382, 111941.
[36] Wang, Z. M., Sahle-Demessie, E., Aly Hassan, A., & Perrett, C. (2012). Surface Structure and Photocatalytic Activity of Nano-TiO 2 Thin Film for Selective Oxidation. Journal of Environmental Engineering, 138(9), 923-931.

*Corresponding Author | Abdul Manaf, N. A. | azlian@upnm.edu.my

[37] An, W. J., Thimsen, E., & Biswas, P. (2010). Aerosol-chemical vapor deposition method for synthesis of nanostructured metal oxide thin films with controlled morphology. The Journal of Physical Chemistry Letters, 1(1), 249-253.
[38] Varshney, G., Kanel, S. R., Kempisty, D. M., Varshney, V., Agrawal, A., Sahle-Demessie, E., ... & Nadagouda, M. N. (2016). Nanoscale TiO2 films and their application in remediation of organic pollutants. Coordination Chemistry Reviews, 306, 43-64.
[39] Arabatzis, I. M., Antonaraki, S., Stergiopoulos, T., Hiskia, A., Papaconstantinou, E., Bernard, M. C., & Falaras, P. (2002). Preparation, characterization and photocatalytic activity of nanocrystalline thin film TiO2 catalysts towards 3, 5-dichlorophenol degradation. Journal of Photochemistry and Photobiology A: Chemistry, 149(1-3), 237-245.
[40] Fujishima, A., Rao, T. N., & Tryk, D. A. (2000). Titanium dioxide photocatalysis. Journal of photochemistry and photobiology C: Photochemistry reviews, 1(1), 1-21.
[41] Noh, M. F. M., Teh, C. H., Daik, R., Lim, E. L., Yap, C. C., Ibrahim, M. A., ... & Teridi, M. A. M. (2018). The architecture of the electron transport layer for a perovskite solar cell. Journal of Materials Chemistry C, 6(4), 682-712.
[42] Tung, W. S., & Daoud, W. A. (2011). Self-cleaning fibers via nanotechnology: a virtual reality. Journal of Materials Chemistry, 21(22), 7858-7869.
[43] Kim, E. H., Lim, M. H., Lah, M. S., & Koo, S. M. (2018). Synthesis and characterization of heteroleptic titanium MOCVD precursors for TiO 2 thin films. Dalton transactions, 47(7), 2415-2421.
[44] Patil, M. K., Shaikh, S., & Ganesh, I. (2015). Recent advances on TiO2 thin film based photocatalytic applications (a review). Current Nanoscience, 11(3), 271-285.
[45] Eufinger, K., Poelman, D., Poelman, H., De Gryse, R., & Marin, G. B. (2007). Photocatalytic activity of dc magnetron sputter deposited amorphous TiO2 thin films. Applied surface science, 254(1), 148-152.
[46] Begum, N. S., & Farveez Ahmed, H. M. (2008). Synthesis of nanocrystalline TiO 2 thin films by liquid phase deposition technique and its application for photocatalytic degradation studies. Bulletin of Materials Science, 31, 43-48.
[47] Karuppuchamy, S., Suzuki, N., Ito, S., & Endo, T. (2009). A novel one-step electrochemical method to obtain crystalline titanium dioxide films at low temperature. Current Applied Physics, 9(1), 243-248.
[48] Pore, V., Rahtu, A., Leskelä, M., Ritala, M., Sajavaara, T., & Keinonen, J. (2004). Atomic layer deposition of photocatalytic TiO2 thin films from titanium tetramethoxide and water. Chemical Vapor Deposition, 10(3), 143-148.
[49] Yemmireddy, V. K., & Hung, Y. C. (2017). Using photocatalyst metal oxides as antimicrobial surface coatings to ensure food safety—Opportunities and challenges. Comprehensive Reviews in Food Science and Food Safety, 16(4), 617-631.
[50] Kang, S. M., Jang, S., Lee, J. K., Yoon, J., Yoo, D. E., Lee, J. W., ... & Park, N. G. (2016). Moth-Eye TiO2 Layer for Improving Light Harvesting Efficiency in Perovskite Solar Cells. Small (Weinheim an der Bergstrasse, Germany), 12(18), 2443-2449.
[51] Mauchauffé, R., Kim, J., Kim, D. H., Lee, S., Kwon, M., & Moon, S. Y. (2021). UV-Shielding TiO2 thin film deposition on flexible and heat-labile substrate using an open-air hybrid CVD/Plasma method. Vacuum, 192, 110424.
[52] Modan, E. M., & PLĂIAŞU, A. G. (2020). Advantages and disadvantages of chemical methods in the elaboration of nanomaterials. The Annals of "Dunarea de Jos" University of Galati. Fascicle IX, Metallurgy and Materials Science, 43(1), 53-60.
[53] Gaur, D., Sharma, S., & Ghoshal, S. K. (2021). Modified structures, optical and photovoltaic characteristics of low energy ions beam irradiated TiO2/TiO2-Graphene thin films as electron transport layer in perovskite solar cell. Materials Today: Proceedings, 43, 3826-3832.
[54] Putri, A. A., Abuelwafa, A. A., Kato, S., Kishi, N., & Soga, T. (2021). Effect of TiOx and TiO2 layer on the photovoltaic property of BiOI films. Key Engineering Materials, 884, 372-378.
[55] Dongale, T. D., Shinde, S. S., Kamat, R. K., & Rajpure, K. Y. (2014). Nanostructured TiO2 thin film memristor using hydrothermal process. Journal of Alloys and Compounds, 593, 267-270.
[56] Dulian, P., Nachit, W., Jaglarz, J., Zięba, P., Kanak, J., & Żukowski, W. (2019). Photocatalytic methylene blue degradation on multilayer transparent TiO2 coatings. Optical Materials, 90, 264-272.
[57] You, M. S., Heo, J. H., Park, J. K., Moon, S. H., Park, B. J., & Im, S. H. (2019). Low temperature solution processable TiO2 nano-sol for electron transporting layer of flexible perovskite solar cells. Solar Energy Materials and Solar Cells, 194, 1-6.
[58] Khan, M. I., Bhatti, K. A., Qindeel, R., Althobaiti, H. S., & Alonizan, N. (2017). Structural, electrical and optical properties of multilayer TiO2 thin films deposited by sol–gel spin coating. Results in physics, 7, 1437-1439.

*Corresponding Author | Abdul Manaf, N. A. | azlian@upnm.edu.my

[59] El Haimeur, A., Makha, M., Bakkali, H., Gonzalez-Leal, J. M., Blanco, E., Dominguez, M., & Voitenko, Z. V. (2020). Enhanced performance of planar perovskite solar cells using dip-coated TiO2 as electron transporting layer. Solar Energy, 195, 475-482.
[60] Tahir, M. B., Riaz, K. N., Hafeez, M., & Fidous, S. (2017). Review of morphological, optical and structural characteristics of TiO2 thin film prepared by sol gel spin-coating technique. Indian Journal of Pure & Applied Physics (IJPAP), 55(10), 716-721.
[61] Sławek, A., Starowicz, Z., & Lipiński, M. (2021). The influence of the thickness of compact TiO2 electron transport layer on the performance of planar CH3NH3PbI3 perovskite solar cells. Materials, 14(12), 3295.
[62] Mandati, S., Veerappan, G., & Ramasamy, E. (2022). Large area bar coated TiO2 electron transport layers for perovskite solar cells with excellent performance homogeneity. Solar Energy, 240, 258-268.
[63] Dadashbeik, M., Fathi, D., & Eskandari, M. (2020). Design and simulation of perovskite solar cells based on graphene and TiO2/graphene nanocomposite as electron transport layer. Solar Energy, 207, 917-924.
[64] Ebrahimi, M., Kermanpur, A., Atapour, M., Adhami, S., Heidari, R. H., Khorshidi, E., ... & Rezaie, B. (2020). Performance enhancement of mesoscopic perovskite solar cells with GQDs-doped TiO2 electron transport layer. Solar Energy Materials and Solar Cells, 208, 110407.
[65] Liu, X., Wu, Z., Zhang, Y., & Tsamis, C. (2019). Low temperature Zn-doped TiO2 as electron transport layer for 19% efficient planar perovskite solar cells. Applied Surface Science, 471, 28-35.
[66] Cai, Q., Zhang, Y., Liang, C., Li, P., Gu, H., Liu, X., ... & Shao, G. (2018). Enhancing efficiency of planar structure perovskite solar cells using Sn-doped TiO2 as electron transport layer at low temperature. Electrochimica Acta, 261, 227-235.
[67] Arshad, Z., Khoja, A. H., Shakir, S., Afzal, A., Mujtaba, M. A., Soudagar, M. E. M., ... & Saeed, M. (2021). Magnesium doped TiO2 as an efficient electron transport layer in perovskite solar cells. Case Studies in Thermal Engineering, 26, 101101.

*Corresponding Author | Abdul Manaf, N. A. | azlian@upnm.edu.my