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An Investigation for Electron Transport Layer Material for Efficient Perovskite Solar Cell

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Abstract

In perovskite solar cell (PSC) technologies, the electron transport layer (ETL) plays a significant role. Despite the fact that ETL-free planar-type PSCs have been reported, their highest Power conversion efficiency (PCE) is only 14.14 percent, much lower than that of ETL-containing cells, illustrating the necessity of the ETL in this configuration of PSCs. For high device efficiency, an appropriate ETL should meet a few basic parameters. For example, good optical transmittance to ensure that enough light is transmitted into the perovskite absorber, matched energy levels with perovskite materials to produce the expected open-circuit voltage (Voc), and high electron mobility to effectively extract carriers from the active layer to avoid charge recombination. In planar-type PSCs, fast carrier extraction is desired to limit charge accumulation at the interface due to ion migration and eliminate hysteresis. Thus, for high PCE devices, the focus has been on building high-quality ETLs with appropriate energy levels and high electron mobility. This paper, covers electron-transporting layer-free construction, features of electron transporting layer, and techniques to improve ETL performance using a variety of materials such as TiO_2, ZnO, SnO_2, EDTA, E-SnO_2, and WO_3.

Keywords: Solar cell; Perovskite; Stability; Renewable energy; Power conversion efficiency; Thin films.

Introduction

In the twenty-first century, energy scarcity has become a global issue. The majority of the world's energy is now derived from fossil fuels such as coal, petroleum, and natural gas, which are finite and have negative health and environmental repercussions. The desire to develop renewable energy sources such as hydroelectric, geothermal, wind, and solar to replace fossil-fuel-based energy generation has sparked a lot of study. Solar energy is one of the most promising renewable energy solutions for meeting expanding global energy demands and resolving or mitigating the ever-increasing energy problem caused by the depletion of fossil fuels [1]. Solar power is expected to become the most major source of energy by 2050, while accounting for only 1% of total energy production in 2013 [2]. Solar energy has several key advantages over other renewable technologies, including global sunlight distribution (as opposed to localized wind,

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geothermal, and hydroelectric resources), the lack of hazardous waste generation (as opposed to nuclear energy), and the decentralized nature of solar energy generation [3].

Because of their hybrid nature (inorganic and organic), low production costs, and better power conversion efficiency, perovskite solar cells (PSCs) have gotten a lot of interest in recent years. However, we all know that in order for a product to be commercialized, it must meet certain requirements and criteria. A perovskite is essentially any ABX_3 compound [4]. (where A: alkyl group B: metal and X: halogen). The broad electron diffusion length, high optical absorption, and low processing temperature make it ideal for solar cells [5]. Because of these characteristics, it is expected that its efficiency will surpass that of traditional Si-solar cells in the next years.

Perovskite solar cells are made up of five main components: (a) a metal cathode, (b) a hole transport layer (HTL), (c) an absorber layer, and (d) an electron transport layer (ETL) (f) TCO (Transparent Conductive Oxide), as shown in Fig.1. The transport layer determines a PSC's performance. The HTL collects holes from the absorber layer and transports them to the cathode, preventing electrons from passing through. The electron transport layer (ETL) collects electrons from the absorber layer and transports them to the anode, where they are blocked.

In order to assure electron collection and transport from the absorber layer to the respective electrodes, the ETL layer must be present in an efficient PSC. Using the ETL layer in PSC, on the other hand, boosts the electron-hole pair recombination resistance at the cost of a modest increase in series resistance (Rs). To improve the performance of ETLs, two methods could be used: first, by altering the ETL structure, and second, by using materials with higher optical and electrical properties [6]. In all PSC devices, ETL plays a critical role. As a result, for an effective PSC, a suitable selection of acceptable ETL material is required. Different materials for ETL have been summarized in this study, including TiO_2, ZnO, SnO_2, EDTA, E-SnO_2, and WO_3. The free structure of the electron transporting layer, the features of the electron transporting layer, and methods for improving ETL performance are also explored.

Electron-transporting layer-free structure

For traditional planar perovskite solar cells, a compact n-type metal oxide on the transparent conductive oxide (TCO) is always required, since it aids in achieving high open-circuit voltage (V_{OC}) and overall power conversion efficiency. Hu et al., on the other hand, developed a surface modification technique that used a cesium salt solution to change the indium–tin–oxide (ITO) surface and maximize energy level alignment at this interface, resulting in a Power conversion efficiency (PCE) of 15.1 percent [7]. Later, Liu et al. constructed a compact layer-free PSC with a 13.5 percent efficiency by depositing the perovskite layer directly on the ITO surface using a sequential layer deposition approach,

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proving that an ETL is not required to achieve exceptional device efficiencies [8]. After developing an efficient ETL free PSC with a PCE of 14.14 percent and a V_{OC} of 1.06 V grown directly on an FTO substrate via a one-step solution process without any hole-blocking layers, Ke et al. suggested that a TiO_2 electron-transporting material might not be an ideal interfacial material [9]. Fig. 2 depicts the ETM layer-free planar perovskite solar cell architecture.

Characteristics of electron transport layer

Despite the fact that ETL-free planar-type PSCs have been described [9,10], their highest PCE is only 14.14 percent, which is much lower than that of ETL-containing cells, illustrating the necessity of the ETL in this configuration of PSCs. For high device efficiency, an appropriate ETL should meet several basic conditions [11]. For example, good optical transmittance to ensure that enough light is transmitted into the perovskite absorber, matched energy levels with perovskite materials to produce the expected open-circuit voltage (Voc), and high electron mobility to effectively extract carriers from the active layer to avoid charge recombination, among other things. In planar-type PSCs, fast carrier extraction is desired to limit charge accumulation at the interface due to ion migration and eliminate hysteresis. Thus, for high PCE devices, the focus has been on building high-quality ETLs with appropriate energy levels and high electron mobility.

PSC's ETL is usually an n-type semiconductor (metal oxide) nanostructure that facilitates electron injection from the perovskite into the metal oxide. The most significant property of an ETL is that it must align with the perovskite layer in terms of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) above the perovskite active layer. It must have a high UV-Vis transmittance so that a photon can readily travel through and be absorbed by the perovskite absorber. Exciton production across the perovskite layer via light absorption must be separated before being collected by the ETL or HTL. Savenije et al. [12] revealed the exciton dissociation mechanism. At the ETL/perovskite or perovskite/HTL interfaces, excitons can be separated.

The electron-transporting material (ETM) must be optimized in order to improve PSC performance. In PSCs, both organic and inorganic materials can be utilized as an ETM; inorganic materials are commonly employed in the standard device architecture, while organic materials are typically used in the inverted device architecture. An ideal ETM must possess several characteristics: it must have an energy level compatible with that of the perovskite material in order to promote photo-generated electron injection and reduce energy losses, and it must have innately high electron mobility in order to enable fast electron transport [13]. Figure 3 depicts the energy levels of some typical inorganic ETLs used in perovskite solar cells. Different ETL materials are discussed as follows :

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1. Titanium Oxide (TiO_2)

Due to its excellent photoelectric characteristics, TiO_2 has been a popular electron transport material in PSC till recently [14]. However, the electron mobility of TiO_2 ETL is too low (ca. 10^{-4} cm^2 V^{-1} s^{-1}) to match the high hole mobility of generally used HTLs (ca. 10^{-3} cm^2 V^{-1} s^{-1}) , resulting in charge accumulation at the TiO_2/perovskite interface, causing hysteresis and decreased efficiency [15].

FTO/compact TiO_2/mesoporous TiO_2 and perovskite composite layer/perovskite top layer/PTAA/Au make up the typical mesoporous-type PSC reported by Yang [16]. For mesoporous-type PSCs, it is well known that mesoporous TiO_2 contributes the most to reducing overall hysteresis [17]. However, fabricating a mesoporous TiO_2 layer frequently necessitates a high-temperature (> 450 °C) annealing process, which consumes a lot of energy and limits its use in flexible devices [18-20]. Planar-type PSCs, in contrast to mesoporous-type PSCs, can be made utilizing a low-temperature, low-cost technique [21]. Planar-type PSCs, on the other hand, typically have poor electron conductivity, high charge recombination, and reduced crystallinity, leading in low PCE and severe hysteresis [22-23].

Through morphological optimization, surface changes, and doping, extensive efforts have been made to generate high-quality TiO_2 electron transport layers (ETLs) with high electron mobility. Lithium (Li) [24-25], Niobium (Nb) [26-27], Platinum (Pt) [28], Sodium (Na) [29], Neodymium (Nd) [30], and Aluminum (Al) [31] are just a few of the elements used to prepare TiO_2 doping layers in PSCs. For example, Liu et al. found that the Li doped TiO_2 ETL improved the performance of mesoporous-structure PSCs, particularly in terms of reducing the hysteresis effect [25].The Pt doped TiO_2 ETL, according to Liao et al., might improve charge carrier extraction and injection efficiency in n-i-p PSCs [28]. Other ions, such as Na, Nb, and transition metal ions [29, 30, 32-34], have been utilized to change TiO_2 surface or passivate defect, minimizing non-radiative recombination. Because of its similar radius to that of titanium, Niobium metal (Nb) is an excellent contender as a doping material for titanium oxide electron transport devices. Yin et al findings showed that Nb doping might improve conductivity and mobility while lowering the trap-state density of TiO_2 ETLs for PSCs [26].

Despite these advancements, a relatively high-temperature (150°C) treatment was required, and substantial hysteresis in PSCs based on Nb-doped TiO_2 was still found. Current density-voltage (J-V) hysteresis is a well-known problem that arises regularly, particularly in planar-structure PSC devices. PSCs can become unstable and PCE can degrade as a result of severe hysteresis. As a result, developing a hysteresis-free PSC using a simple and low-temperature approach is extremely desirable. Yu et al. [35] suggested a simple one-step, in situ, low temperature (70°C) technique for producing hysteresis-free PSCs with a single Nb:TiO_2 compact mesoporous layer that serves as both scaffold and ETL. A compact TiO_2 bottom with nano-pin

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morphology on the surface of the Nb:TiO_2 layer can be used as a scaffold. Due to the collaborative effect of the increased interface surface area caused by nano-pin morphology on the surface and the improved carrier transportation rate due to the presence of Nb, the hysteresis index decreased significantly from 24.39 percent for the PSC based on bare TiO_2 to 3.19 percent for the PSC based on 2 percent Nb:TiO_2 layer. The PSCs were able to attain a fantastic PCE of 19.7% thanks to the high-quality mesoporous layer. Tan et al findings suggest that using chlorine to change the TiO2 microstructure at low temperatures resulted in a promising PCE of 20.1 percent [36].

2. Zink Oxide (ZnO)

Because of its advantages, such as better bulk electron mobility with a sufficient band gap and flexibility in morphological management, as well as low processing temperature, ZnO has been considered one of the most promising alternative materials to replace standard TiO_2 [37]. The flexible substrate's ideal temperature range is between 100 and 150 degrees Celsius [38]. Zinc oxide (ZnO) is a semiconductor material with a large band gap and a similar electrical affinity to TiO_2 [40 39]. ZnO films with outstanding structural quality can be formed at low temperatures (150^oC) [40-41]. When compared to TiO_2, it has several orders of magnitude better electrical conductivity [42-43]. For commercial applications, low-temperature produced sol-gel ZnO film could be a feasible alternative to ETL for PSCs.

Uddin et al. [44] used low-temperature produced sol-gel ZnO as the ETL for perovskite solar cells [45]. Sol-gel ZnO ETL, on the other hand, comprises energy disorder caused trap states due to oxygen chemisorption [46-48]. In these trap states, electron transport hopping causes carrier recombination [46, 49-51]. This is a significant problem with sol-gel ZnO ETL produced at low temperatures. For trap-state passivation, an extra ETL PCBM ([6, 6]-phenyl C61 butyric acid methyl ester) layer was added as an intermediary layer between the low temperature treated ZnO layer and the perovskite layer [51-53].

During the 100^oC annealing session of perovskite film [54], the PCBM buffer layer atop ZnO film has been found to diffuse. PSCs with ZnO/PCBM double layer ETL typically have a low PCE (the highest reported PCE is 12.20 percent) [49]. When compared to pristine ZnO ETL-based PSCs, the short circuit current Jsc of Al doped ZnO ETL-based PSCs is lower [51]. In organic solar cells, surface modification of ZnO using cesium acetate showed improved conductivity properties compared to pristine ZnO film [55]. However, no PSCs with cesium acetate doped ZnO as ETL have been reported. Understanding the effect of bulk alteration of ZnO combined with cesium-based dopants on perovskite solar cells is crucial. For ZnO ETL based devices, the effect on the charge transport property [56-58], hysteresis, and device degradation

processes [59] are key characteristics to understand.

3. Tin Oxide (SnO_2)

SnO_2 has recently been demonstrated as an alternate ETL to TiO_2 due to its better electron mobility and more acceptable energy level compared to perovskite. Ke et al. demonstrated a PCE of 16.02 percent with improved hysteresis [14] using SnO_2 thin film as an ETL in typical planar-type PSCs. To improve the performance of PSCs, SnO_2–TiO_2 (planar and mesoporous) composite layers were produced later [60-61]. It's worth mentioning that Al^{3+}-doped SnO_2 has even greater performance [62]. Following that, a number of technologies for manufacturing SnO_2 thin film, including as solution deposition, atomic layer deposition, chemical bath deposition, and so on [63-65], were developed to improve the performance of planar-type PSCs [66]. SnO_2 nanoparticles were designed as the ETL by Jiang et al., who demonstrated a verified efficiency of 19.9% with very minimal hysteresis [67]. The PCE of planar-type PSCs, however, is still lower than that of mesoporous-type devices, owing to charge accumulation at the ETL/perovskite interface caused by the ETL's limited electron mobility [69]. Increased electron mobility of the ETLs is predicted to result in improved PSC performance.

4. Ethylene diamine tetraacetic acid (EDTA)

Due to its high chelation activity, ethylene diamine tetraacetic acid (EDTA) enables good ETL modification in organic solar cells. With Jsc = 22.10 mA/cm^2, Voc = 1.08 V, and FF = 68.71 percent, the EDTA-based device has a PCE of 16.42 percent. Tiny Jsc and FF, which are connected to low electron mobility and high resistance [69], cause low device performance for the EDTA, and low Voc is induced by a small Fermi energy offset between the EDTA and HTL.

5. EDTA Complexed SnO_2(E-SnO_2)

Because it may send its lone-pair electrons to the unoccupied d-orbital of the transition metal atom, EDTA can react with transition metal oxide to produce a complex [69]. As a result, EDTA was chosen to boost the performance of SnO_2. Li et al. used EDTA to passivate ZnO-based ETL and showed that the organic solar cells performed better [70]. When the EDTA–ZnO layer is utilized in perovskite cells, however, the hydroxyl groups or acetate ligands on the ZnO surface react with the perovskite, resulting in proton transfer reactions at the perovskite/ZnO interface, which results in poor device performance [71].

Despite the great efficiency of the mesoporous-type perovskite solar cell (PSC), its planar-type equivalent has a lower efficiency and hysteretic response. Using an EDTA complexed tin oxide (SnO_2) electron-transport layer, Yang et al. were able to minimize hysteresis and achieve record efficiency for planar-type devices [72]. The Fermi level of EDTA-complexed SnO_2 is more closely aligned with the perovskite conduction band, resulting in a high open-circuit voltage. Its electron mobility is

approximately three times that of SnO2. With low hysteresis, planar-type PSCs with EDTA-complexed SnO_2 achieve a record power conversion efficiency of 21.60 percent (confirmed at 21.52 percent by Newport). Meanwhile, the EDTA-complexed SnO_2 produced at low temperatures achieves an efficiency of 18.28 percent for a flexible device. Furthermore, after 2880 hours of exposure in an ambient atmosphere, unsealed PSCs with EDTA-complexed SnO2 deteriorate only by 8%, and only by 14% after 120 hours of irradiation at 100 mW/cm^2. Furthermore, they discover that when SnO_2 is treated with EDTA, the surface becomes more hydrophilic, lowering the Gibbs free energy for heterogeneous nucleation and resulting in a high-quality perovskite coating.

6. Tungsten Trioxide (WO_3)

As an ETL layer, WO_3 is a highly adaptable material. WO_3 thin films have already been synthesized and published in a number of earlier publications. Its features, including as an adjustable bandgap (2.6–3.5 eV) [73], correspond to a wavelength of 475 nm, allowing it to absorb visible light. It also has a noticeable transmittance of (80%) [74] in the visible area, giving the traditional TiO_2 layer a run for its money. In addition, WO_3 has a high conductivity on the order of 10^{-3}/Ω-cm and has n-type semiconductor characteristics [75].

The quantum efficiency curve for WO_3 is almost identical to those of ZnO and TiO_2, paving the door for a new ETL layer that is both cost-effective and simple to produce [76]. The 1.8 eV energy barrier at the CuI/Perovskite interface precludes light electron transport from perovskite to HTL, and the barrier between the perovskite valance band and WO_3 prevents hole flow from perovskite to ETL. As a result, all of these barriers, as well as proper band alignment, play a critical role in improving the device [77]. Figure 3 depicts a band alignment diagram for several ETL layers. In this diagram, ITO serves as a front contact beneath which are various ETL layers with clearly visible band alignment. A perovskite layer is formed by the mixed halide intrinsic perovskite ($CH_3NH_3PbI_3$). Based on simulation findings, it was discovered that WO_3 can be an excellent alternative for TiO_2 since it has a higher short circuit current and PCE than TiO_2 (as given in Table 3). It has a high level of electron mobility. Controlling the oxygen content during deposition or processing can adjust its density of states and Fermi level. Temperature affects the crystal structure of WO_3. It exhibits a stable monoclinic form at room temperature [78].

Approaches to improve performance of ETL

Modifications of metal oxide CTL deposition methods and/or deposition conditions, doping, surface treatments, interface modifications and/or interfacial layers, and other procedures investigated to increase PSC performance often work on the following mechanisms: (a) increased charge collection, (b) decreased interfacial traps/recombination losses, and (c) improved perovskite layer quality placed on top of the CTL.

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Conclusion

Though many inorganic and organic ETLs have been employed in PSCs, this review will focus on inorganic ETM systems. When compared to organic/polymer ETL/HTL, inorganic ETL/HTL has a greater electron/hole diffusion length. According to one study, hybrid solar cells do not require an HTL but do require an ETL/scaffold . As a result, for an effective PSC, a suitable selection of acceptable ETL material is required. The reported PCE for TiO_2 is 20.48, ZnO is 21.01, SnO_2 is 18.93, EDTA is 16.40, E-SnO_2 is 21.60, and WO_3 is 21.85, as indicated in the table. However, multiple ETL layers were utilized, and the most effective ETL layer was found to be WO_3.

In compared to other ETL layers, WO_3 has a higher power conversion efficiency than any other ETL layers, albeit other aspects must be taken into account. The WO_3-based PSCs are extremely temperature sensitive; a rise in PSC temperature alters material conductivity, causing PV characteristics to degrade. Developing low-temperature manufactured electronics will thus be a viable direction and trend in the future.

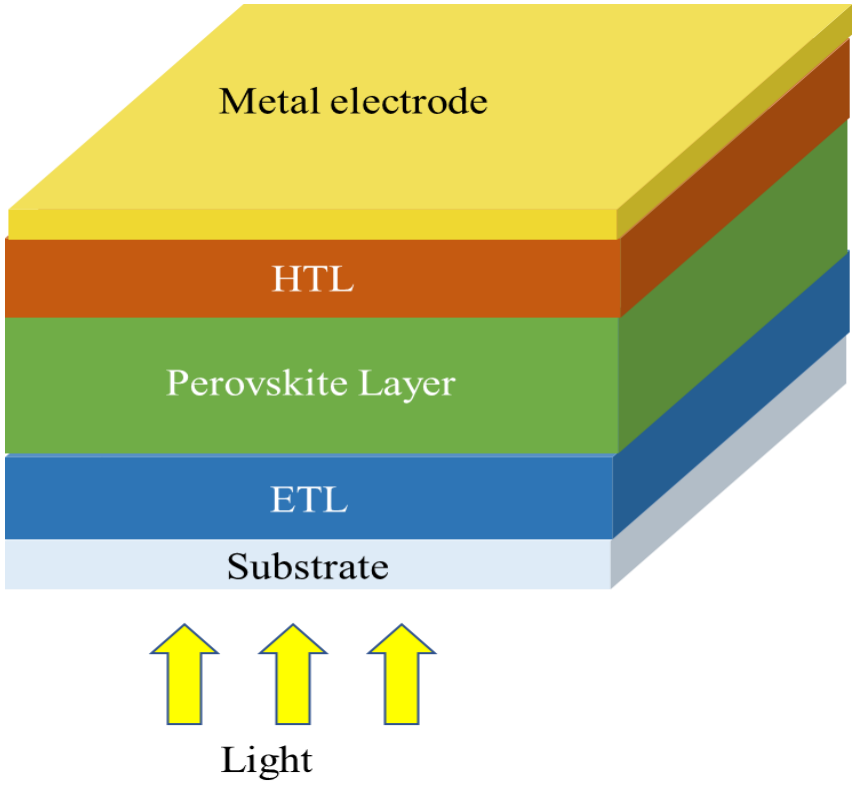

Fig. 1 Schematic diagram of general device.

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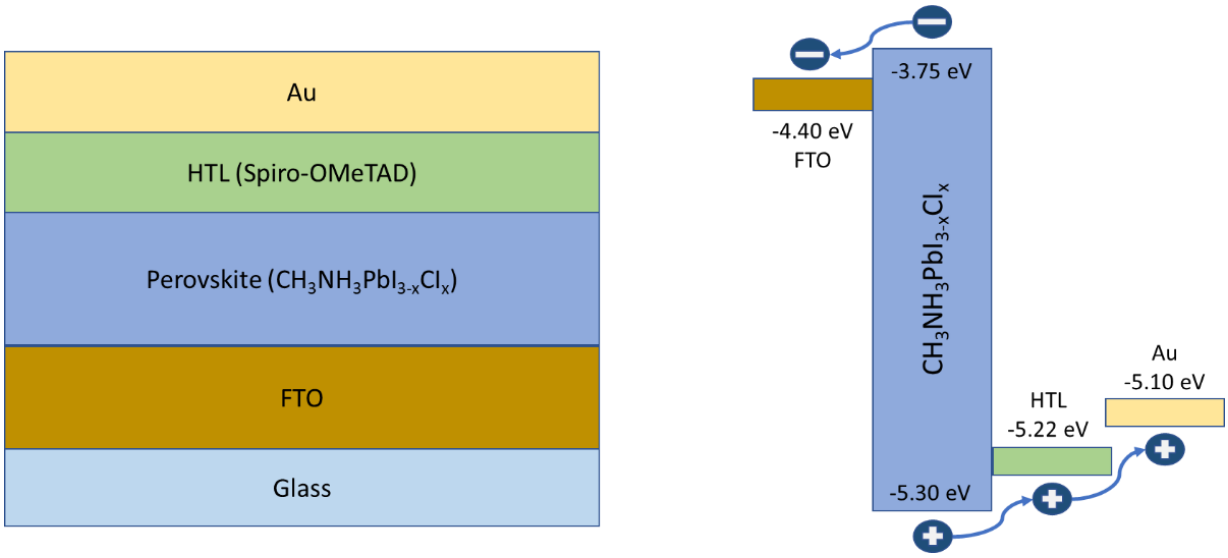

Fig 2 - (a) Schematic illustration of the electron transport layer-free planar mixed halide perovskite solar cell configuration and (b) energy level diagram of the planar PSC showing collection and separation of photo-generated electrons and holes without an ETL [79].

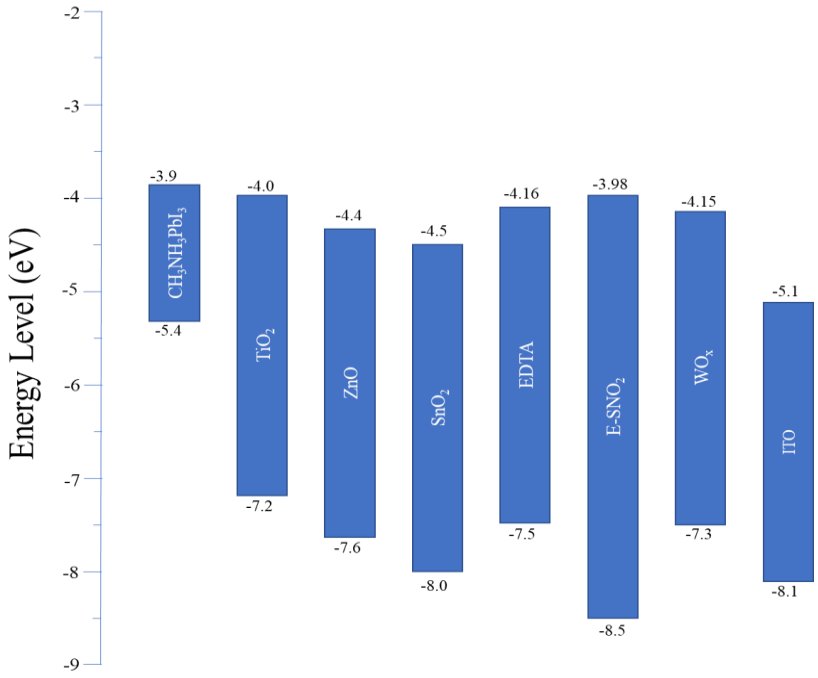

Fig 3 - Energy levels of different materials acting as inorganic ETM with varying layers of perovskite solar cell

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Conflict of Interest : The author declare that they have no conflict of interest.

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