

Composition of Electron Transport Layers in Organic Solar Cells (OSCs).

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Abstract. The research on organic solar cells has attracted researcher attention because of their flexibility, low cost and relatively simple processing methods. However, the efficiency issue is the shortcoming of organic solar energy, and one of the key factors affecting the power conversion rate is the utilization of electron transport layer. Among the materials used for the electron transport layer, metal oxides are widely used due to their stability, ease of preparation and tunable energy band structure. This article review the advantages and disadvantages of metal oxides as electron transport layers particularly focus on SnO₂, TiO₂ and ZnO. The different nanostructures properties of the materials is also explores. A brief discussion on the use of metal oxides as electron transport layers in improving the performance of organic solar cells in the future is also elucidated.

Keywords: ZnO, Charge Transport, Electron Transporting Layer, Solar cell, Satbility.

1. Introduction

Energy has always been one of the problems facing mankind and at the same time, sustainable energy has always been a major concern and a great challenge. The world's largest source of energy, i.e., the sun is one of the many focal points because of the stable technology and lower cost of photovoltaic cells. The photovoltaic effect is a physical phenomenon occurred in the solar devices, by converting the photon energy (light) into electricity. The origin of the photovoltaic effect (1839) was firstly discovered by a German physicist, Edmund Becquerel [1]. Due to the enormous potential of photovoltaic cells and the growing demand for the sustainable energy, it have become one of the trends in research and development.

In the last decade of photovoltaic cell development, inorganic silicon-based solar cells has achieved a major share in the market, especially in 2019 with 90% of growth rate [15]. The low cost of raw materials and proven technology are the biggest attractions of silicon-based solar cells. However, a significant challenges in terms of rigidity, high installation costs and low conversion rates has been reported. There are many researcher is paying the attention to overcome the aforesated issue with various methods. In the year of 2001, the emergence of a flexible organic solar cells has become one of the alternative approach to encounter the problem especially in a power generated flexible device technology. The greenish and low maintenance cost of the raw materials used in manufacture organic solar cells is eventually reduces the long term fabrication costs. There are several methods are introduce such as low-temperature processing and inkjet printing technology [2,3]. Nevertheless, the low device performance of organic solar cells has always been the biggest issue.

A numerous efforts has been introduced by the researcher to improve the performance via investigating on the fundamental electronic transistion state of the photoactive layer, modifying the device archiotecture structure as well as designing a compatible photoactive material. (Plases include the two to three of the previous research finding on the mentioned issue).Lately, a research on the combination of the organic solar cell (OSc) technology with the perovskite solar cells (Psc) is reported. The aim of this study is to increases the device performance in the hybrid solar cell. According to the latest data reported in NREL statistic, the device performance of OSc is sucesfully improve from 2.5% to 18.2% from 2001 to 2020. The summarized of NREL statictic with the best research-cell efficiencies in different solar cells from 1976 to 2022 is depicted in Figure 1. Although

the device performance is greatly, while the stability of the device is abruptly decreases. This matter had limited the development of sustainable device in long term operation.

The basic structure of organic solar cell consists of five important layer which are cathode, anode, electron transporting layer (ETL), photoactive layer and hole transporting layer (HTL). Numerous study has been conducted in modifying the photoactive layer- a majority photon absorbed layer that determining the carrier concentration in the device. In another note, the ETL also plays a crucial role in the operation of organic solar cells. The ETL is design between the cathode layer and the photoactive layer. Its fundamental role is (i) to maintain the electron transport between the electrode layer and the photoactive layer, (ii) act as a barrier to prevent mutual inetraction between the layers and (iii) regulates the energy level of the electrode and the photoactive layer. Among the type of organic solar cells, bulk heterojunction junction (BHJ) structure is commonly used. There are several study has been reported on the incorporation of metal halide element such as lithium fluoride (LiF) or caesium carbonate (Cs_2CO_3) into the active material, aiming to increase the carrier concentration in the conventional OSC. However, the addition of halogen cation is proved to reduce the lifetime of the OSC. Therefore, a focus of the study is later switch to the design of inverted based OSC structure.

An attention has been focus on the properties of ETL layer. A common maetrial used in the transition layers is zinc oxide (ZnO), tin oxide (SnO_2) and titanium dioxide (TiO_2) due to its intrinsic properties such as good photon absorption in UV-Vis region as well as feasible modification in optical energy bang structure. Comparatively, TiO_2 is selected because of its broad energy band, high stability and excellent optical properties whereas ZnO material does not require a high-temperature syntehsis, which provide another merit for the selection. In contrast, the defect rich nature in the ZnO nanostructure has limited the accessibility for fabricating a stable device. Lately, SnO_2 is well-established owing to the high transmission, conductivity and low-temperature processing material that suitable for OSC fabrication [4]. The fundamental study on the electron transpoting mechanism in different ETL is important to further understanding and improve the device performance.

In align with the highlight issue, herein, a short review on the general operation principle of organic solar cell (OSC), type of OSC, properties of electron transporting layer (ETL), selection of ETL in determining the devie performance is prepared. A future perspective and suggestion on the organic solar cell development also included.

2. Overview on Operating Principle in Organic Solar Cells

2.1. Device premeter of OSC

The current density-voltage (J-V) curve is an important analysis in determining the solar cells device performance. The schematic diagram for the basic J-V curve is depicted in Figure 2 [8]. The J-V characteristic of the devices is divided into two analysis conditions whiure are (i) stationary illuminated environment and (ii) dark system. There are three important parameter can be obtained from the J-V curve namely open current circuit (V_{oc}), short circuit current (J_{sc}) and fill factor (FF). In detail. V_{oc} , this denotes the highest voltage that a solar cell is capable of supplying to an external circuit. J_{sc} , this comes when the voltage throughout the device is zero and is the maximum current that a solar cell can produce. FF provide the information on the power conversion efficiency (PCE) of OPV. It determines the extent to which the solar cell deviates from the ideal diode and also indicates the maximum power exhibited from the fabricated solar cell.

The J-V caharacteristic of the device is derive from the equivalent circuit of the solar cell. The schematic diagram for the equivalent circuit of the ideal solar cell and the practical solar cell is depicted in Figure 3. In an ideal solar cell, there is no external load resistance and resulting to an efficient conversion of photon energy into a current. This process presented a 100% FF. For the experimental testing, Thus, the constant current environment is added, which is used to simulate the photo-generated current density (J_{ph}). During the device performance characteristic, a n external loaded which is diode is introduced to provide the uni-directional current flow which eventually ascribed to the shape of the J-V curve. Therefore, the fill factor of the practical solar cell is showing

the lower FF. In practical solar cell equivalent circuit, the connection of series resistance (R_s) and the shunt resistance (R_{sh}) is form. The R_s is referred to the (i) resistance between the active layer bulk and the bulk of the electrodes or (ii) the resistance between the active layer and the electrodes. The R_{sh} is reflected by the pinholes or the defect in the device that leading to the leakage current. For the week performed devices, researcher is looking for the low R_s and high R_{sh} value.

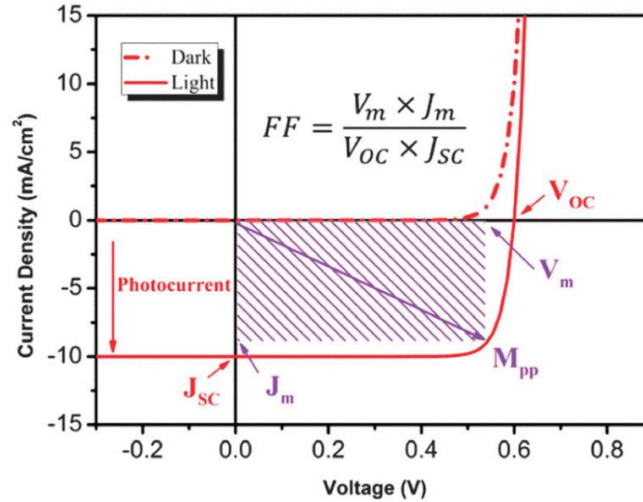


Figure 1. The schematic of typical current-voltage characteristics for dark and light conditions in a solar cell illustrates the important parameters for such devices: J_m and V_m are the current density and voltage at the maximum power point (Mpp) [8].

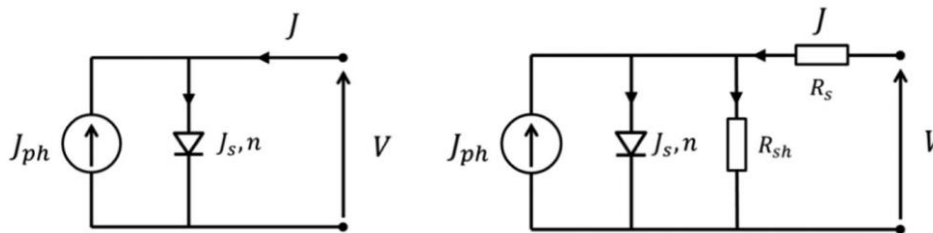


Figure 2. The schematic shows the equivalent circuit: the left panel is the ideal solar cell equivalent circuits, the right panel is the practical solar cell equivalent circuit [5].

3. Properties of Electrode Transporting Layer

There are three main types of nanostructures in solar cells: zero-dimensional, one-dimensional and two-dimensional. The zero-dimensional structures are mainly quantum dots and nanoparticles, the one-dimensional structures are mainly nanowires, nanorods, nanotubes and nanoribbons, etc. The most common two-dimensional structures are multilayer thin films and ultra-thin films. [6]

The most common structures of metal oxide materials used in electron transport layers are: nanoparticle structures, nanorod structures, branched nanorod structures, and porous single-crystal structures. The schematic diagram for the different nanostructures of metal oxide is depicted in Figure 3. A suitable nanostructure determines a higher surface area and better electron transport, and therefore the efficiency of such solar cells, taking the most common ZnO materials as an example: the nanolayer structure of ZnO, the long and thin nanowire structure is the ideal structure for ZnO, in order to obtain more surface contact area and therefore better electron transport efficiency, the vertical structure of the dendrites has a more efficient result, however, the structure also has corresponding disadvantages such as gaps between the branches, which are extremely prone to photon crossing and photon losses. Therefore, on the basis of the branched nanorod structure, a multi-vacancy single-crystal structure was created, in which the number of voids is reduced and has more charge collecting surfaces. [7]

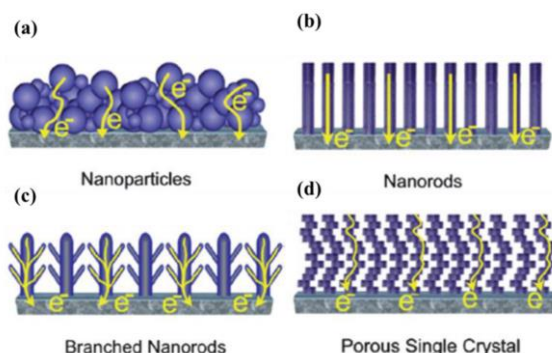


Figure 3. The schematic is present the different nanostructures of metal oxide.

4. Comparisons from methodologies and materials

4.1. Fabrication methodologies and result

ZnO is the most used material for electron transport layers and has been studied for the longest time with the best experimental methods, as its Fermi energy level matches the energy level of LUMO very well. ZnO is a direct wide band gap material with an energy band of 3.37eV and also has a strong high exciton binding energy at room temperature, resulting in a ZnO material with excellent and good optical properties. Not only that, but organic solar cells with ZnO have higher shunt resistance values. ZnO can be formed in a variety of nanostructured forms, and different nanostructures are produced by different synthesis methods such as chemical vapour deposition (CVD), sol-gel, electrodeposition (ED), vapour-liquid-solid (VLS), etc. The schematic diagram for the different nanostructures of ZnO is depicted in Figure 4.

As an example of nanorod structures generated by the sol-gel method, the first step is the solution-gel method, in which zinc acetate is first mixed with 2-methoxyethanol, a stabiliser (e.g. MEA) is added, then heated and finally placed in a drying oven for 24 hours for ageing. Once the solution is prepared, it is evenly spin-coated onto the substrate. The second step is hydrothermal growth to synthesise the zinc oxide nanorods, which is done in the growth solution.

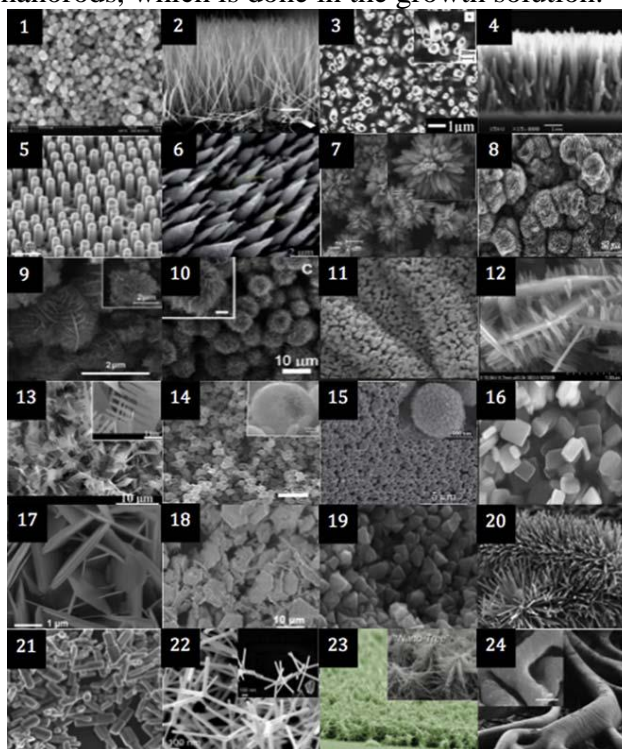


Figure 4. The schematic is present the different nanostructures of ZnO.[13]

TiO₂ is of interest due to its extremely wide energy band gap, tolerance, non-toxicity and low cost, with a band gap of approximately 3.2 eV. Figure 5 depicts a schematic of the band gap of different materials between MOHO and LUMO for organic solar cells. However, TiO₂ is not a very desirable material for electron transport layers compared to other metal oxide materials. Due to its metal oxide properties (wide energy gap), this material has almost negligible absorption in the visible spectrum and does not produce high maximum Voc values [9]. However, TiO₂ is greatly and widely used in DSSCs as an anode to absorb incident light. [14]

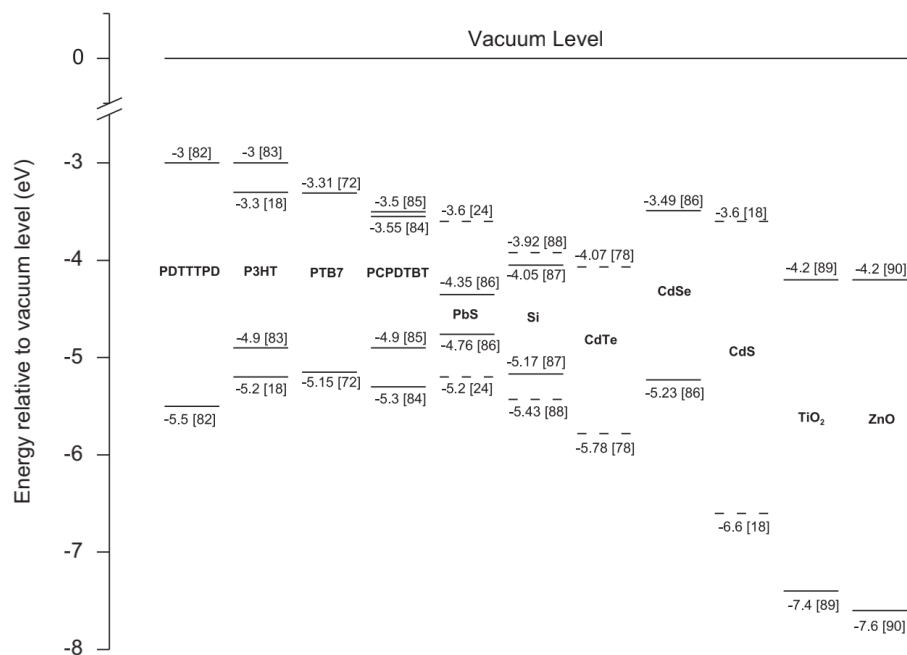


Figure 5. The schematic shows the different materials in the organic solar cell's bandgap between the MOHO and LUMO.[10]

SnO₂ has the lowest CB of these metal oxides materials, SnO₂ has an energy band of about 3.6eV, this semiconductor material has the advantage of high transparency and high electrical conductivity, can be operated at low temperatures and has good optical properties, among the various nanostructures of SnO₂, it was shown that the nanoparticle structure is with good surface area, making the nanoparticle structure have better photon absorption and scattering capabilities. The specific synthesis method for SnO₂ nanoparticles, produced by a sol-gel process, consists of dissolving tin chloride dihydrate in ethanol and spinning the prepared solution uniformly onto the substrate. Finally, the spin-coated substrate is annealed.

In SnO₂ materials, the main factor affecting the efficiency of electron transport is the nanoparticle structure, while the main factor in nanoparticle structure is the temperature of annealing.

The bilayer is a combination of crystalline and amorphous, worthwhile by a low-temperature solution process. Surface morphology can be improved, and electron recombination reduced.

4.2. Comparisons

In a comparison of different electron transport layers, it can be found that SnO₂ as an electron transport layer material combines all the advantages of ZnO and TiO₂. SnO₂ has bandgaps between 3.5eV and 4.0eV, effectively connecting the photoactive layer to the electrode layer and effectively reducing electron recombination. In addition, Xiong et al. in 2020 found [4] that SnO₂ has excellent glass transmittance compared to TiO₂, which has good optical properties, with visible light transmittance up to 95%. The schematic diagram for transmittance comparison between the TiO₂ and SnO₂ on the FTO substrate is depicted in Figure 6. SnO₂ is thus the most desirable material among metal oxides.

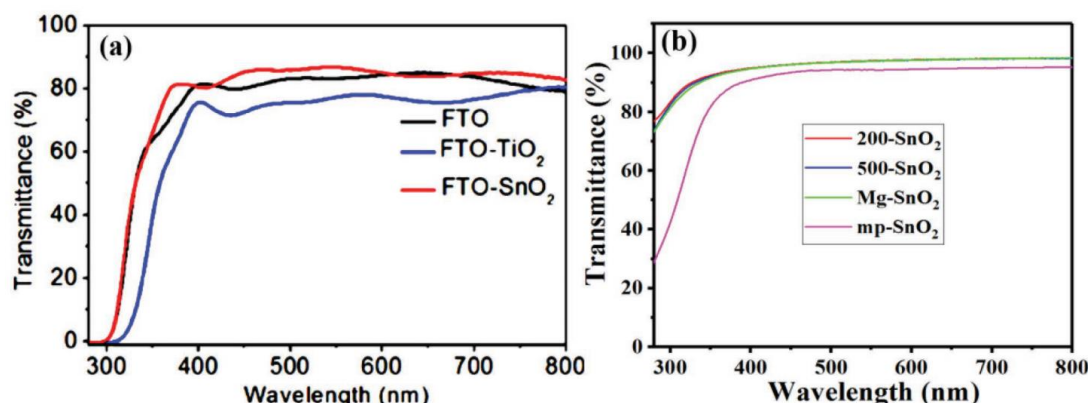


Figure 6. The diagram on the left shows the comparison of transmittance between the TiO₂ and SnO₂ on the FTO substrate [11], the right one is shown the transmittance of SnO₂ on a glass substrate. [12]

In recent years, more and more researchers, instead of studying the electron transport layer of one material alone, have combined multiple transport layers, taking SnO₂ as an example. The bilayer's SnO₂ is a combination of amorphous SnO₂ and crystalline SnO₂. On the surface, the bilayer has more contact area and also has a higher surface area to volume ratio.

5. Limitations & Future outlooks

The biggest problem with organic solar cells is their low conversion efficiency compared to chalcogenide solar cells. The main reasons for this are divided into the following areas: (1) At the source, not all photons are accepted, i.e. the photon loss. (2) The electron pairs do not move sufficiently to the donor-acceptor surface after excitation. (3) The loss of recombination during the movement. (4) Inadequate collection of charge carriers arising from low electron mobility.

A top priority for the future development of organic solar cells should be to improve the stability and conversion rates of organic solar cells, for example by mixing newly designed materials with different organic solar cell structures, or the lifetime of the raw material can be improved by different manufacturing methods, for example by introducing different types of encapsulation methods to minimize losses. Large-area installations of organic solar cells are also a future direction to explore for commercial and market applications. As well as on the artificial side, devices with ductility and flexibility also hold great promise.

6. Conclusions

In summary, this paper discusses the electron transfer layers of different materials in organic solar cells from the perspective of the optical properties of the transfer efficiency. Specifically, the optical properties of the electron transfer layers and the materials themselves are compared for the three materials, ZnO, SnO₂ and TiO₂. According to the analysis, the electron transport layer made from SnO₂ has excellent optical properties and in addition is easier to fabricate compared to the other two materials. In the future, the light conversion efficiency of organic solar cells will be improved and the prospects for applications on the market are very promising. Overall, these results provide guidance for the enhancement of organic solar cells.

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