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Improving Dye-Sensitized Solar Cells Photocurrent Performance based on Titanium Dioxide Photoanode Thickness

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ABSTRACT

The thickness of the photoanode film in dye-sensitized solar cells (DSSC) is a crucial parameter for optimum power conversion efficiency. The thick film can provide a high generation rate of a free electron, and at the same time, the charge recombination of electrons also increases. Therefore, there is competition between electron generation and charge recombination, which can cause the decreased performance of the DSSC. Meanwhile, the thinner film can reduce the charge recombination, but the dye loading on titanium dioxide (TiO_2) will be low, which also can downgrade the DSSC performance. Therefore, optimised thickness from the current-voltage characteristic to understand the effect of thickness on efficiency and photocurrent generation. The result shows that the optimum thickness is 3 layers of scotch tape with short-circuit current density and efficiency of 10.96 mA/cm^2 and 3.81 %.

1. Introduction

Solar electricity or photovoltaic (PV) is a technology that permits a direct conversion from sunlight to electrical energy without the emission of greenhouse and other pollution. The PV cells can be categorized into three generations depending on the operational principle, fabrication techniques, and type of materials. The first-generation PV cells is based on crystalline silicone wafers and the oldest and frontier in PV technology due to its high conversion efficiency. The second-generation PV cells are commonly called thin-film PV cells due to cells are made from layers of semiconductor materials with micrometer and nanometer thickness. The typical materials for the second-generation materials are cadmium telluride (CdTe) and copper indium gallium selenide (CIGS). However, there are some drawbacks of CdTe which are toxicity of cadmium (Cd) and abundant of telluride (Te) which

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are true concern for large scale production [1]. In addition, the price of indium (In) used in CIGS cells increases due to the high demand of In element in liquid crystal display and touch screen devices which are the main concern for large scale CIGS cell production [2,3]. Recent research in third-generation PV has been focused on manipulating nanomaterial to improve the light harvesting and power conversion efficiency of PV devices. The dye-sensitized solar cells (DSSC) introduced by Grätzel and O'Regan in 1991 was a breakthrough discovery in the PV field. DSSC device basically employs dye molecules between the two different electrodes. The DSSC typically comprises of four components: semiconductor photoanode, usually titanium dioxide (TiO_2), dye-sensitizer, electrolyte, and a counter electrode. The advantage of the DSSC device is the less complexity of the fabrication process, where the electrode can be fabricated using a doctor blade and screen-printing techniques without using high technology equipment and expensive equipment. Besides that, high flexibility, transparent and low cost of manufacturing are also the main attraction of the DSSC device.

The heart of device, photoanode layer composed of mesoporous semiconductor material deposited on transparent conductive oxides substrates either using doctor blade, screen printing, spin coating or RF sputtering [4-7]. The semiconductor material used in DSSC is a metal-oxide group, typically TiO_2 where photoanode layer contained mesoporous metal-oxide that is used for holding dye-sensitized molecule and also as an electron transporter from the dye. Therefore, a large surface area for dye adsorption, wide bandgap, high electron mobility, and chemical stability are some of the major requirements for selecting photoanode material in DSSC [8]. The TiO_2 is selected as the photoanode material due to the wide bandgap semiconductor of 3.0-3.2 eV depending on the phase structure. There are three phase structures of TiO_2 which is anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). However, anatase is the most preferred structure in DSSC because of wider bandgap energy of 3.2 eV compared to rutile 3.0 eV [8]. This can lead to higher Fermi energy level and open circuit voltage (V_{oc}) for the same conduction band electron concentration. Besides that, in grain structures, the rutile phase appears in rod-like structure compares to anatase with spherical structure. This structural advantage can be related to the surface area of mesoporous which is, the rutile has low surface area than anatase that can reduce the surface density and porosity that can affect the adsorption of dye onto the TiO_2 [9]. Other than that, the TiO_2 is chemically inert, non-toxic and environmentally safe giving the reason why TiO_2 is selected as photoanode material. Besides that, the higher surface area of TiO_2, especially in anatase phase, can serve for dye anchoring, high electronic mobility for photogeneration of electron, and TiO_2 able to adjust the band edge for electron injection from most of the dye-sensitizers gives an advantage to the TiO_2.

The thickness of the photoanode layer is required to optimize in order to have optimum power conversion efficiency. The thick film can increase the electron generation and at the same time, increasing the electron recombination thus reducing efficiency [10]. Meanwhile, thin film can help reduce the electron recombination, but also reduce the dye loading on TiO_2 which can also reduce the efficiency. Hence, the optimal thickness is required to encounter the electron recombination in DSSC modules. In this paper, the optimum thickness was studied from the current-voltage (I-V) characteristic performance in order to understand the effect of thickness on the efficiency and photocurrent generation.

2. Methodology

2.1 Preparation of TiO_2 Photoanode Paste

All the chemical were used as purchased from the manufacturers without any further purifications. TiO_2 (anatase, < 25 nm), ethyl cellulose and α-terpineol were purchased from Sigma Aldrich.

TiO_2 paste were prepared by modified Vesce and Riccitelli [11] technique. Prior to the preparation, the TiO_2 powder was sintered at 450 °C for 30 min to remove any moisture and inorganics impurities. At each step, ethanol was added into porcelain mortar and the TiO_2 slurry that stick on the pestle should be removed by plastic spatula in order to grind large aggregates. The used of steel spatulas should be avoided during paste preparation to prevent surface contamination by iron cations that can induced charge recombination in DSSC module. Then, the TiO_2 dispersion was ultra-sonicated for 30 min for better dispersion of TiO_2 into the paste. α-terpineol and ethyl cellulose in ethanol was added, followed by stirring for 24 hours at 70 °C. The TiO_2 paste was slowly evaporated until it reached a suitable viscosity for the deposition process. The uses of α-terpineol make the paste suitable for deposition process on the fluorine doped tin oxide (FTO) glass and lengthen paste shelf life, and for ethyl cellulose is to tunes paste viscosity, rheology, and porosity, leaving vacancies after sintering.

2.2 Deposition of TiO_2 Photoanode Layer and Sintering Process

A proper substrate cleaning procedure was followed prior to any deposition, mainly to remove any surface contamination by the other cations on the surface of the substrate which considerably enhances charge recombination in the DSSC. The FTO glass was cut using diamond cutter into 2.5 cm × 2.0 cm pieces. Each of the pieces was cleaned using 1 % detergent solution, de-ionized water, acetone and isopropyl alcohol. At each step, the FTO glass were ultra-sonicated at 10 min. Lastly, the glass was dried in oven at 100 °C for an hour.

Doctor blade technique is the simplest and direct method for depositing TiO_2 paste on the FTO glass. In the experiment, the number of scotch tape layers were used to controlled the thickness of TiO_2 photoanode layer. The Scotch tape (3M, Scotch Magic Tape) with thickness of 52 µm was placed on the edges of the conductive sides to create 1 cm^2 rectangular masking for TiO_2 paste deposition. The TiO_2 paste was then applied on the masked top edge of FTO glass and spread across the unmasked area using microscope slide. After that, the tapes were removed, leaving uncoated area of the FTO glass which used as an electrical contact for I-V measurement. Figure 1 shows the process of TiO_2 paste deposition.

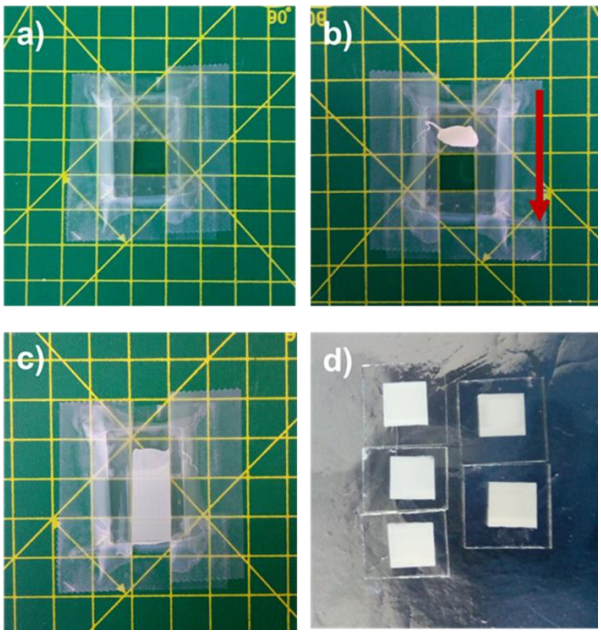

Fig. 1. Step by step process of deposition TiO_2 paste using doctor blade techniques (a) scotch tape were placed on the edges of the FTO glass leaving 1 cm^2 area masking for TiO_2 paste, (b) small amount of TiO_2 paste were applied on top of the edges (c) with the help of microscope slide the TiO_2 paste was spread on the masking area and (d) the scotch tape removes, leaving 1 cm^2 area of TiO_2 film

In the next step, the FTO glass coated with TiO_2 film was sintered at 450 °C for 30 min to remove the presence of organic binder and additives. The temperature is slowly raised from 125 °C to 450 °C for an hour and maintained at 450 °C for 30 min. A sudden increase in temperature may damage the TiO_2 film due to thermal damage. This heating method is crucial to remove organic components, to make the electrical connection between nanoparticles and to obtain a crack-free film. Then afterward the heating is stopped and the film was allowed to cool down until 100 °C. It can be observed that the film was changed from yellowish to white color. After that, TiO_2 film was kept in a sealed petri dish to avoid any adsorption of moisture onto the TiO_2 film. Figure 2 shows the process of sintering and the time step for the sintering process.

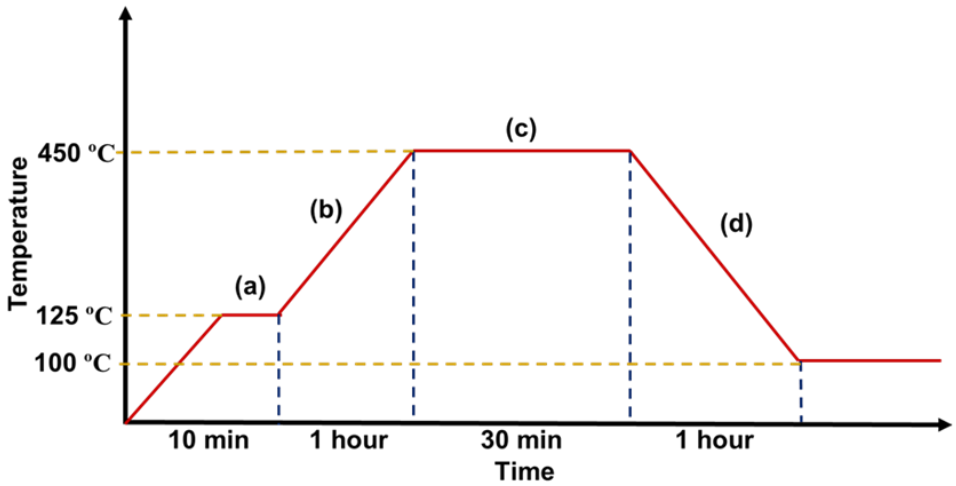

Fig. 2. Time step for sintering process, (a) 125 °C heat treatment to remove ethanol, (b) slow heating process from 125 °C to 450 °C to avoid thermal damage of TiO_2 film, (c) constant heating at 450 °C for 30 min to remove binder and additives and (d) slowly reducing the temperature for 450 °C to 100 °C to cool down the TiO_2 film

2.3 Dye Adsorption and DSSC Assembly

The 0.2 mM N791 dye solution was prepared in acetonitrile and tert-butyl alcohol in equivalent ratio. The dye solution needs to wrapped using aluminum foil to avoid any direct contact from light and required to heat at 80 °C before used for sensitization. The TiO_2 film was immersed in the dye solution and then kept 20 hours at room temperature to adsorb the dye onto the TiO_2 surface. Then, the photoanode was rinsed with ethanol to remove any excess dye. Figure 3 describes the dye adsorption process of TiO_2 film.

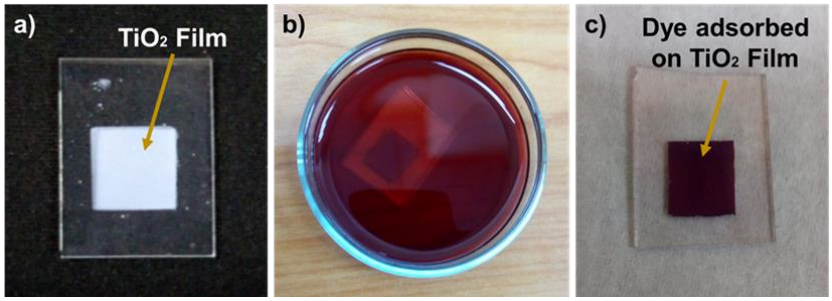

Fig. 3. (a) TiO_2 film after sintering 450 °C, (b) immersion in N719 dye for sensitizing process and (c) TiO_2 film after 20 hours immerse and after rinse with ethanol

3. Results and Discussions

3.1 Morphological Structural of TiO_2

The field emission scanning electron microscopy (FESEM; JEOL, JSM-7800F) images of the TiO_2 on the FTO glass as shown in Figure 4. High magnification images in Figure 4(a) depict that the anatase-TiO_2 particles were spherical-like shapes with nanosize diameter an average of 25 nm. In DSSC, the anatase phase is preferable than the rutile phase due to structural properties. Rutile phase appears in rod-like structure and larger grain sizes than spherical-like anatase particles. This structural can be compared associates to the surface area of rutile is smaller than anatase which can reduce the

surface density and porosity of film [9]. Figure 4(b) displays the low magnification TiO_2 film, it is shown that the doctor blade method able to produce a high nanoporous and dense films. High porosity TiO_2 film is an important aspect that greatly affects the power conversion efficiency. Electron hopped randomly through the spherical connected TiO_2 grain network and take more time in the pathway before they reach the substrates. Thus, high porosity in the grain network can speed up the transport rate of redox mediators in the electrolyte and greatly influence the I-V characteristic [10]. Other than that, high porosity TiO_2 can adsorbs more dye molecules lead to the increase of photogeneration of the electron [10].

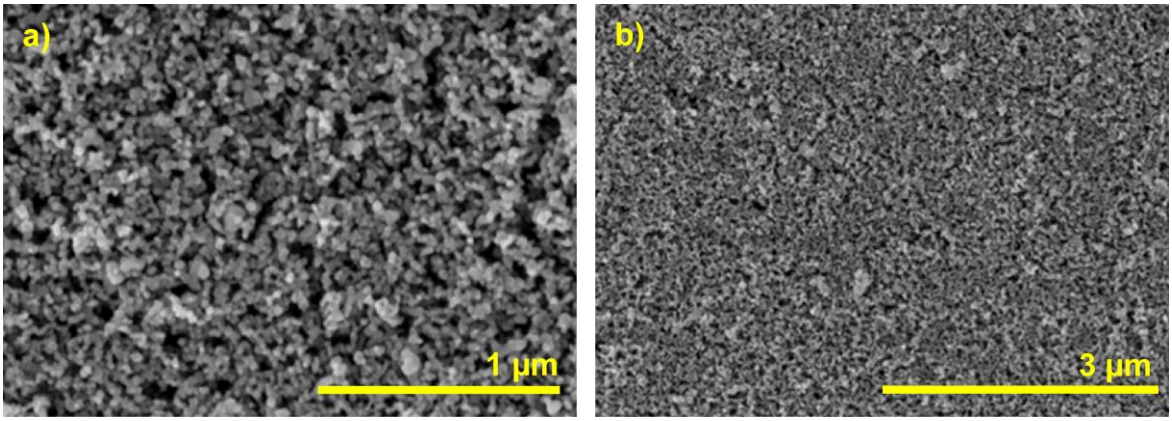

Fig. 4. FESEM images of TiO_2 film deposited on FTO glass using a doctor blade method (a) 40 kX and (b) 15 kX magnification

3.2 Thickness Analysis

The height profile of TiO_2 photoanode film at different layers of scotch tape was shown in Figure 5. The thickness was measured by using a 3D laser measuring microscope (Olympus, OLS4100). For the measurement of the thickness, 410 nm light laser is used to scan 1 cm width of the deposited TiO_2 film. The scanning provides a step difference which necessary for the measurement of thickness. The measured thickness using one layer of scotch tape = 5.28 µm, two layers = 13.46 µm, three layers = 15.15 µm, four layers = 28.72 µm and five layers = 33.80 µm. As shown in Figure 5, the bowl-like shape become more significant as the thickness of scotch tape layer increased. This is due to the center of film drying faster than edges sides during pre-heating process, which can reduce the performance of DSSC due to non-uniform surface.

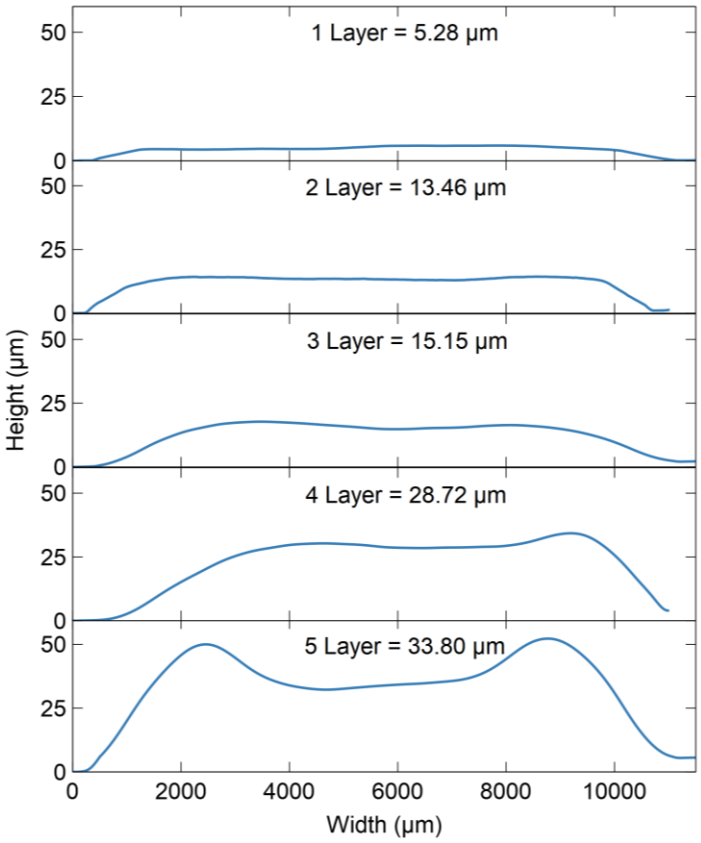

Fig. 5. Height profile for different thickness TiO_2 using the doctor blade method. The measured thickness using one layer of tape = 5.71 µm, two layers = 12.83 µm, three layers = 14.38 µm, four layers = 28.49 µm and five layers = 34.11 µm

3.3 Current-Voltage (I-V) Performance

The comparison of the I-V performance of different TiO_2 film thickness is shown in Figure 6(a). From the graph, we can see that three layers of scotch tape with 14.38 µm thickness resulted in the highest J_{sc} with 10.96 mA/cm^2. Figure 6(b) and Figure 6(c) show the performance of J_{sc} and efficiency at a different scotch tape layer. The J_{sc} is increased from 6.06 to 10.96 mA/cm^2 when the thickness of TiO_2 film increases and started to reduce when the thickness is further increased to more than three layers The efficiency had also followed the same graph trend as J_{sc}, with the highest efficiency of 3.81 % for three layers thickness. These results may be explained by the fact that the increasing of photoanode thickness can affect the improvement of dye loading attached onto the TiO_2 nanoparticles. By means, thicker TiO_2 film can have more number of TiO_2 nanoparticles in per unit area, so, more amount of dye molecules can be adsorbed. Thus, this improved amount of dye can maximize the photon absorption and increased the rate of electron injection from excited dyes to conduction band of TiO_2 as can be seen in the improvement from one to three layers of scotch tape [11,12]. Figure 6(d) reveals that the V_{oc} is slightly increased from 0.60 to 0.63 V when the scotch tape layers increase up to three layers, and the V_{oc} started to decrease when the layers were further increased. The potential difference depends on the energy level of redox mediator electrolyte. The decrement of V_{oc} is caused by the electron recombination at the interface of TiO_2/dye/electrolyte [12,13]. When the thickness increased, an excess electron that generated only cause the electron recombining with electrolyte. However, at the same time, the increasing of thickness will decrease

the amount volume of electrolyte in solar cells due to the space gap for electrolyte reduced. This only can cause a problem for electron regeneration that leads to lowering the V_{oc}. As shown also in Figure 6(e), the highest fill factor (FF) was found at the three layers, with FF value of 55.0 %. As the TiO_2 film grew thicker, the FF value began to decrease. The increasing of FF could be due to the higher generation of a free electron in the TiO_2 film, which was causing an increase in maximum power point [14]. Thus, it was concluded that the optimum thickness is three layers of scotch tape in order to have the highest photocurrent generation and power conversion efficiency.

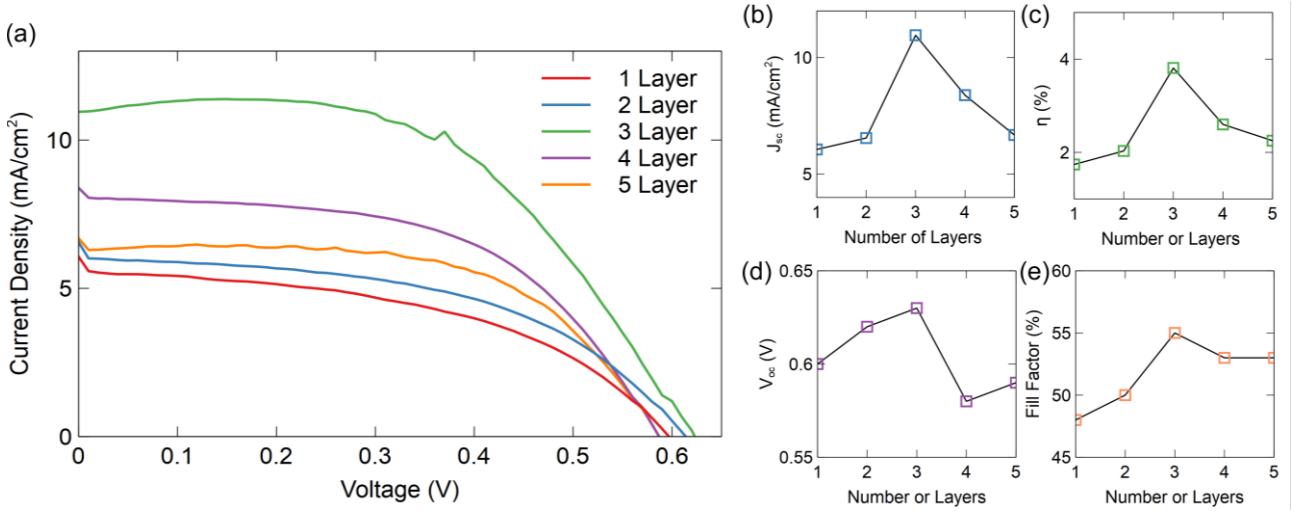

Fig. 6. (a) Current-Voltage characteristics, (b) short-circuit current density, (J_{sc}), (c) efficiency (η), (d) open-circuit voltage (V_{oc}), and (e) fill factor (FF) at different number of photoanode layer

Furthermore, as the scotch tape layer is increased to more than four layers, we expected that the efficiency will increase as more dye molecule attached onto TiO_2, however interestingly, the efficiency is reduced by 2.60 and 2.25 %. This problem related to the electron transfer through the TiO_2 nanoporous network. As we know under light illumination, charge transfer happens at the dye/TiO_2 interface through electrons in the dye being injected into the conduction band (CB) of TiO_2 and then, electron travel by hopping from one TiO_2 nanoparticle to the next before reached FTO conducting glass [13]. Figure 7 depicts the scheme of electrons transfer as the thickness increased. Other than that, increasing of J_{sc} and efficiency while increasing the thickness from one layer to three layer also causing the rising of an electron lifetime in the TiO_2 film in which related to the electron transport in the TiO_2/dye/electrolyte. But, further increase to four and five layers, only can lead to an increase in the loss of injected electrons due to the charge recombination in the electron transfer process in TiO_2 nanoporous network that resulting to the decrease in photocurrent generation and power conversion efficiency [15].

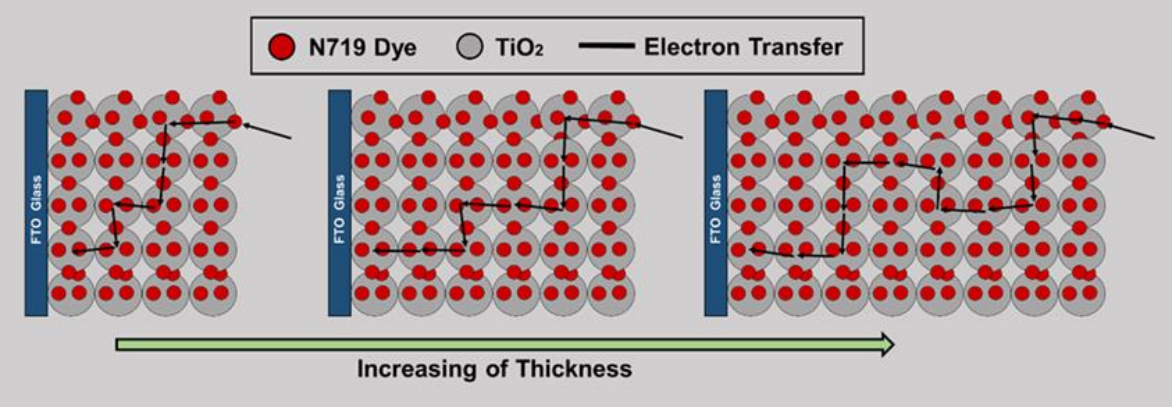

Fig. 7. Electron transfer mechanism in the TiO_2 nanoporous network at different thickness

4. Conclusions

In summary, the present study proposed the method to enhanced light absorption for improvement of J_{sc} and efficiency by optimizing the thickness of TiO_2 photoanode film. The TiO_2 were deposited using doctor blade technique on the FTO glass. The thickness of the TiO_2 film were controlled by the number of layers of scotch tape. The optimum thickness of TiO_2 for this experiment is 3 layer of scotch tape with J_{sc} and efficiency of 10.96 mA/cm^2 and 3.81 %. This indicates that this thickness can improved the light absorption and meanwhile, electron recombination was able to be reduced leading to the increase in photogeneration.

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