Optimization of Titanium Dioxide Layer Fabrication Using Doctor Blade Method in Improving Efficiency of Hybrid Solar Cells

Nurul Huda Kamarulzaman¹⁴, Hasiah Salleh²*, Ahmad Nazri Dagang¹, Mohd Sabri Mohd Ghazali³, Nurhayati Ishak¹, Zakiyah Ahmad⁵

¹ School of Ocean Engineering, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia
² Centre for Fundamental and Liberal Education, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia
³ School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia
⁴ Faculty of Applied Sciences, Universiti Technology MARA, 23200, Dungun, Terengganu, Malaysia

*hasiah@umt.edu.my

Abstract. Hybrid solar cell (HSC) in a form of novel photovoltaic is considered among promising research topic due to its low cost’s preparation and environmental friendly solar cells. This paper concerns a systematic study on concentration of TiO₂ and effect of coating techniques towards solar cells’s efficiency. However, this paper is limited to doctor blade and spin coating techniques only. These samples were then characterised based on morphology, thickness, optical absorption, electrical conductivity and solar cell’s efficiency using various techniques including FESEM, profilometer, UV-Vis and, autolab with irradiance of 100 mW/m². From the results, TiO₂/PEDOT:PSS with dye Eugenia clavifora (EC) obtained the highest efficiency of 1.33% using doctor blade technique compared to 0.00108% for spin coating technique. Sample thickness was obtained at 60.25 ± 1.20 nm corresponding to the concentration of TiO₂ at 0.20 M. Thus, it can be conclude that, power conversion efficiency (PCE) was dependent to the deposition techniques of the thin film.

1. Introduction

Past few decades shows that, reliable and cost effective technologies are the most promising solution to this world energies crisis. Thin film photovoltaic is one of the major concerns in commercial applications. The sufficient thickness required for thin film from fractions of a nanometer (monolayer) to 100 micrometers. Galium arsenide (GaAs), cadmium telluride (CdTe) and titanium dioxide (TiO₂) are the three most widely commercializes thin film solar cells. Inorganic materials seem to be promising in studying the effect on photovoltaic performance in heterojunction. Metal oxide semiconductor consists of TiO₂, ZnO [3, 14], CuSO₄ [7] and FeO₃ [5] have been studied extensively in hybrid solar cells (HSC). Among them, TiO₂ is the most promising acceptor material for hybrid solar cells, owing to its environment-friendly and availability. Titanium dioxide nanoparticle is widely used as photo anode inorganic semiconductors to improve the electron transport through the film [21]. Furthermore, inorganic semiconductors are commonly regarded as the most viable due to its high
electron mobility together with good physical and chemical stability. The combination with conjugated polymers are comprises of their flexibility and low cost in large scale production.

HSC in the form of novel photovoltaic is considered as a promising research topic due to its low cost’s preparation and environmental friendly solar cells. Meanwhile, stability and low cost preparation of HSC are related to its thin film fabrication and coating method. Fabrication of thin film have been prepared via low temperature deposition technique from solution. Several method and techniques required to synthesis thin film including Physical Vapour Deposition (PVD), evaporation, electrodeposition, electrochemical method, spin coating, doctor blade and screen printing. In order to prepare low cost photoanode in HSC, doctor blade, spin coating and screen printing are the most preferable. The realibility of these techniques is a concern to improve the performance of products and functional system [16]. However, this choice of preparation methods should be based on actual situation.

Deposition layers may be applied depending on the process, thickness and roughness requirement. According to Chonsut et.al, doctor blade technique offer thicker film by increasing deposition speed [4]. This thickness of thin film was observed to be in the range of 26 nm to 148 nm which is generally acceptable in thin film application. Chonsut et.al also mentioned that the roughness obtained from doctor blade techniques exhibits similar properties to those obtained in spin coated film [4]. Therefore, manufacturing cost in fabrication process can be reduced. Similar results have been reported by Wantana, which mentioned that, the film surface was becoming smoother when the speed was increased [19]. Interestingly, from previous researches, it was found that, solar efficiency for both techniques (doctor blade and spin coating) were slightly less different in value [19]. Therefore, both techniques are suitable to be used to obtain high quality multilayer thin films for solar cells. Meanwhile, doctor blade is more suitable for fabrication of ultrathin film and may affect the film nanostructures.

The main objectives of this paper is to investigate i) effect of TiO$_2$ concentration on its structural, optical and electrical behaviors useful to photovoltaic applications and ii) effect of coating techniques towards solar cells’s efficiency. However, this paper is limited to doctor blade and spin coating techniques only. Advantages and disadvantages for both method can be emphasized which causes selection and optimization of a given method easier. Therefore, to improve efficiency of hybrid solar cell, fabrication process for thin film in nanoscale process is important to be considered.

2. Experimental details

2.1 Materials
TiO$_2$ colloid was prepared by using TiO$_2$ powder (anatase, 25 nm by Sigma Aldrich Chemical) with ethanol (95%, HmbG Chemicals). Different concentrations such as 0.15 M, 0.20 M, 0.25 M and 0.30 M were used in preparation of TiO$_2$. This sample was deposited onto indium tin oxide (ITO) glass using i) doctor blade technique and ii) spin coating technique with 3000 rpm in 10 seconds [1]. These substrates were then annealed for 15 mins at 450 °C on a hot plate to burn out all surfactant and organic binder in order to improve the contact between substrate and coated layer [11] After cooling down these samples to room temperature, sample was transferred to a glove box to avoid contamination. As a conducting organic layer, highly conductive polymer, PEDOT:PSS was coated on the prepared TiO$_2$ film at spinning speed of 2000 rpm for 10 seconds [8, 22].

2.2 Sample preparation and fabrication of hybrid solar cells
EC’s dye was deposited on top of TiO$_2$/PEDOT:PSS film by using dip coating techniques at 5, 10, 15 and 20 minutes. Finally, its back surface, Aluminum (Al) electrode was coated using physical vapour deposition (PVD) to control the evaporation thickness. Scanning electron microscopy (FESEM), have been used for sample imaging and thickness of TiO$_2$ was measured from cross-sectional FESEM images, and cross-checked with surface profiler (Dektak 150 surface, Bruker),UV-Vis spectrometer (Model Lambda 25) has been used for optical characterization and electrical conductivity were
measured with four point probes (FPP). Current-voltage (IV) was obtained using Autolab Potentiostat PGSTAT 302 with 100mWm\(^{-2}\) of light intensity.

3. Results and discussion

3.1. Effect of coating method towards solar cell’s electrical properties

Figure 1 shows IV curve of TiO\(_2\)/PEDOT:PSS obtained from doctor blade techniques and spin coating techniques. As can be seen from Figure 1, efficiency was observed at various TiO\(_2\) concentrations for both techniques. TiO\(_2\) concentration at 0.15 M and 0.30 M for both techniques create negative effect to PCE due to thickness of sample. Related to doctor blade techniques, current is not stable at 0.25 M TiO\(_2\) concentrations, thus effect the efficiency of sample. TiO\(_2\) concentration at 0.20 M exhibits 0.00531% using doctor blade technique. However, sample coated using spin coating techniques at concentration of 0.20 M and 0.25 M were not in contact due to resistivity thus its lower the conductivity.

Therefore, from Figure 1, all TiO\(_2\) concentrations were affected by two factors including thickness and resistivity of sample. If concentration is higher, the thickness of the sample will increase corresponding to low performance of efficiency. Additionally, sufficient thickness can reduce recombination of photogenerated electron formed in semiconductor. Sengupta et.al also agreed with the statement and stated that the adsorption of molecules within semiconductor have to be controlled, electronic charge transport as well as may contribute to enhancement in power conversion efficiency of the device [17].

![Figure 1](image)

Figure 1. A summary of the device performance at 0.15M, 0.20M, 0.25M and 0.30M for the different coating techniques (a) doctor blade (b) spin coating.

Effect of coating method can be observed with resistivities of TiO\(_2\)/PEDOT:PSS sample illustrated in Figure 2. Figure 2 shows resistivities for sample TiO\(_2\)/PEDOT:PSS at 0.15 M and 0.2 M for spin coating method were decreasing with various TiO\(_2\) concentration before increasing at 0.25 M. Then, the resistivity decreased slowly when the film concentration was at 0.30 M. The range of resistivity was between 32 \(\Omega\)cm to 40 \(\Omega\)cm. The resistivity of spin coating techniques were not stable thus the efficiency of sample were affected. However, referring to Figure 2, it shows that the resistivity for doctor blade techniques was in the range of 16.1 \(\Omega\)cm to 19.6 \(\Omega\)cm. Variation of thickness (as measured by TiO\(_2\) concentration) and resistivites tend to decrease slightly from 0.15 M to 0.30M. This happened due to the variation of TiO\(_2\) concentrations which is possibly attributed to a larger crystal grain size that corresponds to a thicker thin film on plates at a high temperature. The temperature was dependence on the exposure of sample under light illumination As a temperature
increases, TiO$_2$ chain becomes excited and hopping inter-chain which acquires faster internal modes with intra-chain ion movements [2]. Therefore, electrical conductivities of the TiO$_2$ increase effectively with the decreasing of resistivity. The resistivity can be determined by [2],

$$R_s = 4.532 \times \frac{V}{I}$$

(1)

where,
RS= sheet resistance (resistivity),
4.532 = correction factor,
V = voltage measured
I = the current applied from the test unit.

Thus, electrical conductivity can be measured as follow;

$$\sigma = \frac{1}{R_s}$$

(2)

where,
$\sigma$ = electrical conductivity
RS = the sheet resistivity.

In addition, the resistivity of films was also affected by different sample preparations.

Figure 2. The resistivity plot for TiO$_2$/PEDOT: PSS samples for a) doctor blade techniques and b) spin coating techniques as a function of TiO$_2$ concentration.

Figure 3 (a) shows the electrical conductivity dependence on concentration of TiO$_2$ thin films. The pattern of electrical conductivity was rapidly increased from dark condition at 0 Wm$^{-2}$ to light condition which is 200 Wm$^{-2}$. The electrical conductivity can be determined using Four Point Probe (FPP) under dark and light radiation. From its results, electrical conductivity was increased under illumination. The highest conductivity was obtained for doctor blade technique at 0.062 ± 6.22x10$^{-4}$ Scm$^{-1}$ for ITO/TiO$_2$ (0.20 M). This sample was measured under light condition with an increment of 1.80% compared to dark condition. Meanwhile, the lowest conductivity was recorded at
0.051 ± 5.09x10^{-4} \text{ Scm}^{-1} for ITO/TiO_2 (0.15 M). This electrical conductivity was observed to increase at 2.21\% under light condition compared to dark condition.

Conductivity for TiO_2 samples for doctor blade techniques and spin coating techniques are shown in Figure 3 (b) as a function of TiO_2 concentration. Figure 3 (b) shows the electrical conductivity under light condition using doctor blade method, was recorded at 0.051±5.09x10^{-4}, 0.062 ± 6.22x10^{-4} \text{ Scm}^{-1}, 0.060 ± 6.02x10^{-4} \text{ Scm}^{-1} and 0.057 ± 5.78x10^{-4} \text{ Scm}^{-1} for TiO_2 concentration of 0.15 M, 0.20 M, 0.25 M and 0.30 M, respectively. By referring to Figure 3(b), the graph clearly shows electrical conductivity increases then decreases with an increases of thickness. Again, 0.2 M sample exhibited the highest electrical conductivity. The electrical conductivity of TiO_2 samples increases gradually and reaches the maximum level at 0.20 M. However, after the concentration increased to 0.25 M and 0.30 M, electrical conductivity decreases rapidly as thin film thickness increase.

The lowest electrical conductivity detected was 0.0167 \text{ Scm}^{-1} for a commercial ITO (0 layer of film) while the highest electrical conductivity for TiO_2 concentration in spin coating techniques were at 0.031 \text{ Scm}^{-1} (0.20 M) and 0.025 \text{ Scm}^{-1} (0.25M). Therefore, the range of electrical conductivity detected was between 0.0167 \text{ Scm}^{-1} to 0.031 \text{ Scm}^{-1}. Meanwhile, the electrical conductivity for 0.15 M and 0.30 M were detected at 0.027 \text{ Scm}^{-1} and 0.028 \text{ Scm}^{-1}, respectively. By referring to Figure 3 (b), the electrical conductivity decreases with the increases of thickness. The electrical conductivity for 0.2 M in dr blade is higher compared to 0.2 m for spin coating sample. Therefore, 0.2 M concentration provides the best electrical performance for different methods under the light condition.

![Figure 3. Electrical conductivity for TiO_2 samples for (a) doctor blade techniques under dark and light illumination and (b) in doctor blade and spin coating techniques.](image)

As we can see from Figure 3(b), electrical conductivity of TiO_2 strongly depends on thickness of the samples [1]. A decrease pattern of conductivity from 0.20 M to 0.30 M was affected by its thickness of the sample. As the thickness of TiO_2 increased, the resistivity was increased [10]. The increment may be due to the lower density of free charge carriers within the material and the increasing of barrier height at grain boundaries [1]. However, an inversely pattern from 0.15 M to 0.20 M suggested due to lack of TiO_2 coated amount. The performance of electrical conductivity can be improved in bilayer heterojunction. Furthermore, this combination in bilayer heterojunction between TiO_2 with other materials can absorbed quite a wide range in solar spectrum. From these results, it can be conclude that, TiO_2 (0.20 M) can be proceed for further investigation in hybrid solar cells.

3.2. Effect of TiO_2 concentration on its optical properties
Spin coating technique obtained poor efficiency compared to doctor blade techniques due to the thickness of sample coated. Spin coating method provides thicker film when rotational speed decrease [4]. The range of 26 – 148 nm of thin film thickness measured from both deposition techniques was
accepted for organic thin film applications [6]. Furthermore, thin films prepared by doctor blade technique at the same thickness of 75 nm shows similar properties to those obtained from spin coated film. However, preparation of thin film by doctor blade technique can significantly reduce the processing material leading to the reduction of manufacturing cost spent in the fabricating process [4]. More than 90% solution wasted due to high centrifugal force in spin coating technique at high speed [19]. One of the significant findings in preparing different concentration of TiO$_2$ was to produce a different thickness of samples using doctor blade method. The thickness was determined at different concentrations of TiO$_2$ layers as shown in Figure 4. As can be seen from Figure 4, thickness of TiO$_2$ films were increased by the increasing of concentration. The thickness was obtained at 46.95 ± 0.93 nm, 60.25 ± 1.20 nm, 92.49 ± 1.84 nm and 107.95 ± 2.05 nm corresponding to the concentration of TiO$_2$ at 0.15 M, 0.20 M, 0.25 M and 0.30 M, respectively.

![Figure 4. Thickness of the bilayer thin film ITO/TiO$_2$ NCs (X) (X=0.15M, 0.20M, 0.25M, 0.30M)](image)

The higher absorption spectra were recorded at different concentrations as shown in Figure 5. Optical characterization of 0.15 M to 0.30 M TiO$_2$ thin films was obtained by UV-Vis in the wavelength range of 250 nm to 380 nm. Previous research stated that wavelength of TiO$_2$ was recorded 380 nm in the ultraviolet (UV) light spectrum [11, 20]. Samples showed high transparency in visible region and a sharp fall in UV region. TiO$_2$ was recorded at various concentrations to determine the best concentration in achieving higher PCE. These concentrations were inversely proportional to the film thickness because of optical losses when a photon transmits through the film[12]. Thus, large amount of photon energy can be absorbed by active layer of TiO2 thin film and contributed to the enhanced power conversion efficiency of the devices [9].

Figure 5 shows ITO/TiO$_2$ (0.20 M) possess the highest UV-Vis absorption followed by UV-Vis absorption for concentration of 0.25 M and 0.30 M. Concentrations of 0.30 M present the lowest absorption among the other concentrations. Wantana stated that at 0.30 M, TiO$_2$ thin film was developed into a dense film due to the increment of light absorption [19]. Absorption for 0.20 M concentration is higher due to the electron–hole pairs in TiO$_2$ solution as shown in Figure 5. Therefore, the electrons in TiO$_2$ molecules exhibit enough energy and become excited to jump from valence band to conduction band and will be leaving positive holes in the valence band [1]. It was also agreed by Lourduraj, the increasing of TiO$_2$ concentration with absorption spectrum of the prepared TiO$_2$ films improves the absorbance behavior of TiO2 films due to the high density of TiO$_2$ particles [13].
Furthermore, the higher absorption value in the visible region reveals that more photon energy will be absorbed by its active layer. Thus, more excitation of electrons into the conduction band of TiO$_2$.

The optical band gap can be determined using Tauc’s plot which includes absorption coefficient and energy of incident light.

$$\frac{(Ahv)^2}{hv-E_g}$$

Figure 5 also presents the optical band gap in a range of 3.45 – 3.60 eV at different concentrations of TiO$_2$ thin films. The optical band gap energy of TiO$_2$ films are obtained from the extrapolation of the graph in Figure. The optical band gap energy for 0.15 M, 0.2 M, 0.25 M and 0.30 M are 3.6 eV, 3.45 eV, 3.48 eV and 3.58 eV, respectively. The direct transition of electrons obtained between the edges of the valence band and the conduction band. The value of the optical band gap energy decreases with the increase of TiO$_2$ concentration except for 0.15 M.

![Figure 5](image)

(a) Absorption spectrum of TiO$_2$ onto ITO substrate (b) energy gap of TiO$_2$ at different concentration: 0.15 M, 0.20 M, 0.25 M and 0.30 M.

3.3. Comparison of power conversion efficiency (PCE) of TiO$_2$/PEDOT:PSS with and without dye.

The effect of coating method can also be observed towards efficiency of TiO$_2$/PEDOT:PSS/dye EC for doctor blade method and spin coating method as mentioned in Table 1. From the results, TiO$_2$/PEDOT:PSS with dye Eugenia clavifora obtained the highest efficiency of 1.33% using doctor blade technique compared to 0.00108% for spin coating technique. TiO$_2$/PEDOT: PSS with dye EC was expected to perform better compared to TiO$_2$/PEDOT:PSS without dye EC. This is also related to its thickness of TiO$_2$ sample. The concentration was related to thickness of sample. As can be seen from the table, efficiency of TiO$_2$/PEDOT:PSS with dye obtained at 1.33% using doctor blade compared to 0.005 % without dye using spin coating.

In nature, the increasing efficiency sample with dye in doctor blade technique was due to existence of anthocyanin which is acting as accessory pigments to the broadening of UV-Vis spectrum and light harvesting capabilities. This is caused by dye EC which act as an insulator to the current flow and the resistance increased as dye EC in the mixture increased. Therefore, with dye EC sample exhibits the best electrical performance compared to TiO$_2$/PEDOT:PSS without dye. From this observation, it can be conclude that, dye EC has an important role in changing the performance of solar cell in terms of efficiency and conductivity. The decreasing film thickness will improve the photocurrent through sensitizer [18].
Table 1. The efficiency of TiO$_2$/PEDOT: PSS with and without dye EC in different coating method a) doctor blade method and b) spin coating method for 0.2 M TiO$_2$ concentration.

| Samples                  | TiO$_2$ concentration | Doctor blade | Spin coat |
|--------------------------|-----------------------|--------------|-----------|
| TiO$_2$/PEDOT:PSS        | 0.20                  | 0.005        | 0.00495   |
| without dye EC           |                       |              |           |
| TiO$_2$/PEDOT:PSS        | 0.20                  | 1.33         | 0.00108   |
| with Dye EC              |                       |              |           |

3.4. Surface morphology (FESEM)

Figure 6 (a) shows FESEM images of the fabricated TiO$_2$ (nanostructure) and their corresponding morphologies: before coating with PEDOT: PSS and natural dye. Surface morphologies and cross section of TiO$_2$ structure were observed at 30 kX magnification. The particle size are estimated to be in a range of 60 nm to 100 nm. Figure 6 (b) shows the cross section image of TiO2 which was deposited on the surface of ITO glass substrate. The agglomeration of TiO$_2$ was clearly observed under a magnification of 30kX and 50kX due to the existance of water in TiO$_2$. It was also agreed that a higher concentration of solute particle leads to agglomeration\cite{13}. The thickness of TiO$_2$ was measured from the cross section view of each corresponding FESEM micrograph. This thickness was observed to be 60.25 nm.

![Figure 6](image-url)
The fabrication of all devices with thickness for every layer was recorded below than 100 nm and leading to a shorter exciton diffusion length. This shorter exciton length was necessary in connection with strong light absorption and due to this requirement; the interface between electron accepting and hole accepting material received more volume heterojunction. It was also agreed that a higher concentration of solute particle leads to agglomeration [13]. EDS was used in conjunction with FESEM analysis to measure the microanalysis of elemetal constituent on the film. Figure 7 represents (a) EDS spectrum of TiO$_2$ and (b) TiO$_2$.

**Figure 7.** (a) EDS spectrum of TiO$_2$ (b) chemical structure of TiO$_2$.

The atomic content on the samples are Ti and Oxygen. Indium (In) and Sn (Stanum) were referring to ITO surface. Si (Silica) refers to glass substrate. The chemical structure for TiO$_2$ was presented in Figure 7(b). Table 2 recorded mass percentage of all elements in the TiO$_2$. Oxygen and Titanium were detected to confirm that TiO$_2$ were the only phase present.

**Table 2.** The mass percentage Titanium Dioxide.

| Element | Energy (keV) | Mass (%) |
|---------|-------------|----------|
| Ti      | 0.3         | 23.8     |
| O       | 0.4         | 24.5     |
| In      | 0.4         | 36.1     |
| Sn      | 0.4         | 0.7      |
| Si      | 0.1         | 8.9      |
| Total   |             | 100      |

4. Conclusion
The variation of thickness as measured by all TiO$_2$ concentrations was studied. Based on comparison with other concentrations, ITO/ TiO$_2$ (0.20 M) obtained the highest UV-Vis absorption followed by 0.25 M and 0.30 M. The resistivity was found to decrease with an increase in TiO$_2$ concentration. The electrical conductivity was also increased under illumination with the highest conductivity obtained at $0.062 \pm 6.22 \times 10^{-4}$ S cm$^{-1}$ for ITO/ TiO$_2$ (0.20 M). The electrical conductivity of ITO/ TiO$_2$ (0.20 M) under light condition also was increased about 1.80% compared to dark condition. From these results, it can be conclude that, TiO$_2$ (0.20 M) can be used for photovoltaic applications.
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