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Analysis of Nanoporous Semiconductor Film Thickness Effect on Short Circuit Current Density of β-Carotene Dye based DSSC: Theoretical and Experimental Approach

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S Solehudin[1], M Diantoro[1*], and A Hidayat[1]

[1.] Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, 5 Semarang Street, Malang, 65145, Indonesia

***E-mail:** markus.diantoro.fmipa@um.ac.id

Abstract

Dye-sensitized solar cells (DSSC) made of TiO_2 have received increasing attention since invented by O'Regan and Gratzel in 1991. Some studies have been conducted to determine the effect of the TiO_2 electrode thickness on the DSSC performance. Nevertheless, the effect of the electrode thickness on the *J–V* characteristics, especially the short circuit current density (J_{sc}), has not been adequately addressed. Therefore, in this investigation, parametric analyses were conducted to study the DSSC electrode thickness effect on J_{sc}. Diffusion model was used to derive the equation of nanoporous semiconductor film thickness (d) dependence on J_{sc}. TiO_2 paste was prepared by mixing TiO_2 powder, acetic acid, PEG 6000, and deionized water with 0.3:0.1:0.1:6 mass proportion. The cells *I-V* curve were characterized using a computerized digital multi-meter (Keithley 2400) with a variable load. The cells short circuit current (J_{sc}) data gotten from the *I-V* characterization were plotted as the function of the thickness of TiO_2 films. The result of the data plot was then compared and fitted with the theoretical modelling result. It is apparent that the DSSC performance largely depends on the TiO2 film thickness. The results was also showed that the diffusion model provided mathematically good approximation to describe the dependence of J_{sc} on the film thickness of DSSC.

Keywords: DSSC, diffusion model, film thickness, short circuit current density, β-Carotene Dye

1. Introduction

Dye-sensitized solar cells (DSSC) made of TiO_2 semiconductor have received large attention since O'Regan and Gratzel published their work in Nature in 1991 [1]. The research has been developed rapidly and a large amount of work has been made to rise the device efficiency from 7.1% in 1991 to 13% in 2014, a level which is necessary for commercial use [2]. Dye sensitized solar cells are well known as a cost-effective photovoltaic device because of its cheap materials and simple fabrication process compared with high-cost conventional silicon solar cells [3]. The impurity in the semiconductor of a DSSC causes less effect on the cell performance compared with a conventional P–N junction-based solar cell because the electron injection and recombination processes occur at the TiO_2/electrolyte interface [4], [5], which made the fabrication of DSSC can be more simple and economical. The current research on DSSC was focus on the material manufacture and theoretical modeling for better understanding of the basic working mechanisms [6]–[11].

The diffusion model that simplified the actual DSSC mechanisms with consideration of all the important material properties, cell design parameters, and operational parameters had been developed to obtain an explicit expression for the photocurrent as a function of the film thickness, light absorption coefficient, and light intensity by [12]. Recently, Gomez and Salvador [13] used the same diffusion model to study how the open-circuit photovoltage varied with the film thickness and the light intensity. Several studies have been conducted to determine the effect of the TiO_2 electrode

thickness on the DSSC performance. However, the effect of the electrode thickness on the *J–V* characteristics, especially the short circuit current density (J_{sc}), has not been sufficiently addressed. Therefore, in this investigation, parametric analyses were conducted to study the DSSC electrode thickness effect on J_{sc} and to optimize the thickness for the highest energy conversion efficiency.

2. Device Modeling

Figure 1 shows the working principle of DSSC. The photon is absorbed by the dye (1) and make it excited (2). Electron is injected from the excited dye to the semiconductor film (3) and then diffuse the TCO (4). The electron is then transferred to external load and then reach the counter electrode (5) in which it is transferred to the redox electrolyte (6). To complete the cycle the electron is then used by the electrolyte to regenerates the dye (7). Reaction 1 to reaction 7 are the forward reaction of DSSC. However, in DSSC beside these forward reaction there also backward reaction. The dye probably back from its excited state to its normal state spontanously by emiting photon back (a) without injecting an electron to the semiconductor film. The electrons in the semiconductor film conduction band can recombine with the oxidized dye (b) and the triiodide species of the electrolite (c). In our model the backward reaction that be considered was just the c reaction.

The total electron current density in the semiconductor film of DSSC is

$$j_e = eD_e \frac{\partial n_e}{\partial x} + en_e \mu_e E, \tag{1}$$

where e, E, D_e, μ_e, and n_e are the electron charge, electrical field, electron diffusion coefficient, mobility and density respectively. The first term on the right hand side is the diffusion current and the second term is the drift current. In this approach the drift current was neglected compared to the diffusion current.

The recombination rate of the conduction band electrons R_e to the triiodide species is derived from first order kinetic arguments and by introducing a mean electron lifetime τ_e. The recombination rate is assumed to be proportional to the deviation of electron density n_e from its (dark) equilibrium value

$$R_e = \frac{n_e - \bar{n}_e}{\tau_e} \tag{2}$$

The photon flux is assumed given by

$$\phi(\lambda, x) = \phi_0(\lambda) e^{-\alpha(\lambda)x}, \tag{3}$$

so, the incident photon rate is

$$-\frac{\partial \phi}{\partial x} = \alpha \phi_0 e^{-\alpha x}, \tag{4}$$

and the electron generation rate is

$$G(x) = \eta_{inj}\left(-\frac{\partial \phi}{\partial x}\right) = \eta_{inj}\alpha\phi_0 e^{-\alpha x}, \tag{5}$$

where ϕ_0, α, and η_{inj} is the incident photon flux, absorption coefficient, and electron injection efficiency from excited dye to the semiconductor. In this model the value of η_{inj} is assumed equal to 1 (one photon generate one electron in the photo-anode).

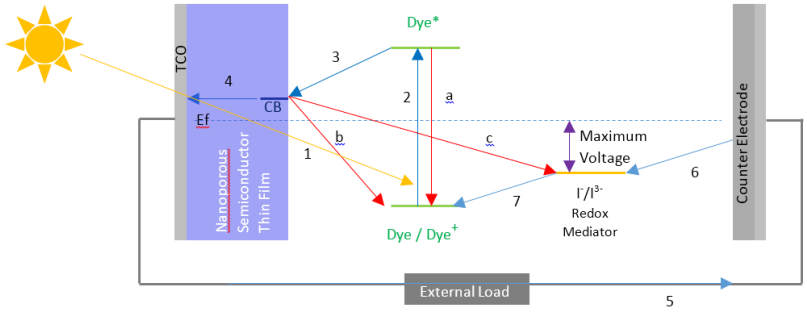

Figure 1. Working principle of DSSC

The continuity equation of the charge carrier number density in the cell is

$$\frac{\partial j_i}{\partial x} + e\frac{\partial n}{\partial \tau} + eG_e(x) - e\,\mathrm{R}_e(x) = 0\,, \tag{6}$$

for steady state equation we have

$$\frac{\partial n}{\partial \tau} = 0\,, \tag{7}$$

so, with neglecting the carrier drift currents, we have

$$\frac{\partial^2 n_i}{\partial x^2} - \frac{n_i - \bar{n}_i}{L_i} + \frac{\phi_0 \alpha \tau_i\, \mathrm{e}^{-\alpha x}}{L_i} = 0\,, \tag{8}$$

with L_i is diffusion length defined as

$$L_i = \sqrt{D_i \tau_i} \tag{10}$$

Solving this differential equation for electron in the conduction band of TiO_2 we get the electron density

$$n_e(x) = n_0 + a\cosh\left(\frac{x}{L_e}\right) + b\sinh\left(\frac{x}{L_e}\right) + \frac{\alpha\phi_0\tau_e}{1-\alpha^2 L_e{}^2}\exp(-\alpha x) \tag{11}$$

Then the current density is

$$j_e(x) = eD_e\frac{\partial n_e}{\partial x} \tag{12}$$

$$j_e(x) = eD\left(\frac{a}{L_e}\sinh\left(\frac{x}{L_e}\right) + \frac{b}{L_e}\cosh\left(\frac{x}{L_e}\right) - \frac{\alpha^2\phi_0\tau_e}{1-\alpha^2 L_e{}^2}\exp(-\alpha x)\right) \tag{13}$$

The *a* and *b* constants can be evaluated using these following boundary conditions

$$n_e(0) = n_{e0} \quad ; \text{without bias} \tag{14}$$

$$\left.\frac{\partial n_e}{\partial x}\right|_{x=d} = 0\,, \tag{15}$$

where n_{e0} is the electron density in equilibrium (dark) condition. The total electron short circuit current density is equal to the current density through semiconductor and TCO boundary (at $x = 0$) without bias, then

$$j_{total} = \frac{e\phi_0 D_e\tau_e\alpha}{(1-D_e\tau_e\alpha^2)}\left[-\alpha + \frac{1}{\sqrt{D_e\tau_e}}\tanh\left(\frac{d}{\sqrt{D_e\tau_e}}\right) + \frac{\alpha\exp(-\alpha d)}{\cosh\left(\frac{d}{\sqrt{D_e\tau_e}}\right)}\right] \tag{16}$$

3. Experimental Details

3.1 TiO_2 Spin Coating Preparation

TiO_2 paste was prepared using same method as Ref. [14]. TiO_2 powder was mixed with acetic acid, PEG 6000, and deionized water with 0.3:0.1:0.1:6 mass proportion. The mixture was sonic bathed for 30 minutes and then stirred at 500 rpm for 2 hours. The TiO_2 solution was spin coated on cleaned FTO glass substrates 5, 10, 15, 25, and 35 times to made 5 TiO_2 films with different thickness. The TiO_2 films were heated at 80 ˚C for 30 minutes and then annealed at 450 ˚C for 1 hour.

3.2 Electrolyte Preparation

The electrolyte was prepared based on Ref. [15]. Acetonitrile (20 ml) was mixed with ethylene glycol (5 ml) and then stirred for 5 minutes. 1.08 gram of KI powder was dissolved in this mixture solvent until homogenous, then 0.21 gram of I_2 crystal was added into this solution. Let the solution be stirred

for 30 minutes to make homogeneous mixture solution of 0.6 mol/L KI + 0.075 mol/L I_2 which gave the optimum support to the cell efficiency based on the result of [15].

3.3 DSSC Fabrication

The TiO_2 films were immersed in β-carotene solution (in absolute ethanol solvent) for 5 minutes and dried at room temperature to make the photo anode. The photo anode was then sandwiched with carbon coated FTO glass (counter electrode). The electrolyte solution was dropped on the slits between the photo anode and the counter electrode and let it diffuse through the photo anode film. The cell then sealed with paper clip binder.

3.4 Characterization and Data Analysis

The thickness of the semiconductor film was measured with ellipsometer measurement and ellipsometry data fitting analysis. Based on Ref. [14], the TiO_2 film thickness from one deposition process was 0.3 μm. From this result, the initial thickness input value for data fitting process of each TiO_2 films was setted to be 1.5, 3, 4.5, 7.5, and 10.5 μm. The cells *I-V* curve were characterized using a computerized digital multi-meter (Keithley 2400) with a variable load. The cells photoelectron current density (*J*) and photovoltage (*V*) were measured with a 0.25 cm^2 active area. The cells short circuit current (*Jsc*) data gotten from the I-V characterization were plotted as the function of the thickness of TiO_2 films which was gotten from ellipsometry fitting result. The result of the data plot was then compared with theoretical graph based on equation (16).

4. Results and Discussions

Based on the ellipsometry data fittting results, the TiO_2 film thickness were 1.5, 3, 4.5, 7.5, and 10.5 μm as shown in Table 1. Figure 2a shows the typical current-voltage characteristics of TiO_2/β-Carotene Dye sensitized DSSC for various film thickness of TiO_2 films. Figure 2b shows the data plot of J_{sc} versus film thickness. It is apparent that the DSSC performance strongly depends on the TiO_2 film thickness. It was found that the J_{sc} was increased rapidly with the increase of film thickness up to 1.5 μm and then decrease slowly as predicted by equation (16).

The dependence of J_{sc} on the film thickness can be explained by the electron photogeneration phenomenon. The increase in electrode thickness directly increases its internal surface area for a given porosity and pore size [16], [17]. Higher internal surface area resulting in a higher dye loading which mean higher photon absorption. These lead to higher electron generation and injection from dye to the semiconductor film. However, if the electrode thickness is larger than the photon penetration depth, the number of photons useful for electron photogeneration will reach the limit and, therefore, J_{SC} cannot be increased any further. Instead, an increase in the thickness beyond the light penetration depth yields more recombination centres that cause a higher electron loss and, thus, a gradual reduction in J_{SC} [18].

The plot of J_{sc} versus film thickness in Figure 2 was seen different with the results of Ref. [19] work which used SnO_2 as the semiconductor film material. This result was also seen different with the results of Ref. [20] and Ref. [21] work which used TiO_2 as the semiconductor film material. The data plot and the theoretical modeling (equation (16)) fitting results of the Ref. [19], [20], and [21] work was shown in figure 3 together with the TiO_2/β-Carotene Dye sensitized DSSC. The practical initial parameters value input for fitting process were listed in Table 2 and the parameters value after fitting process were listed in Table 3. The fitting process was done by using Microcal Origin 6.0 software.

Table 1. The initial input and after fitting value of semiconductor film thickness.

Initial input thickness value (μm)	Thickness value after fitting (μm)
1.50	1.494
3.00	2.998
4.50	4.482
7.50	7.487
10.50	10.492

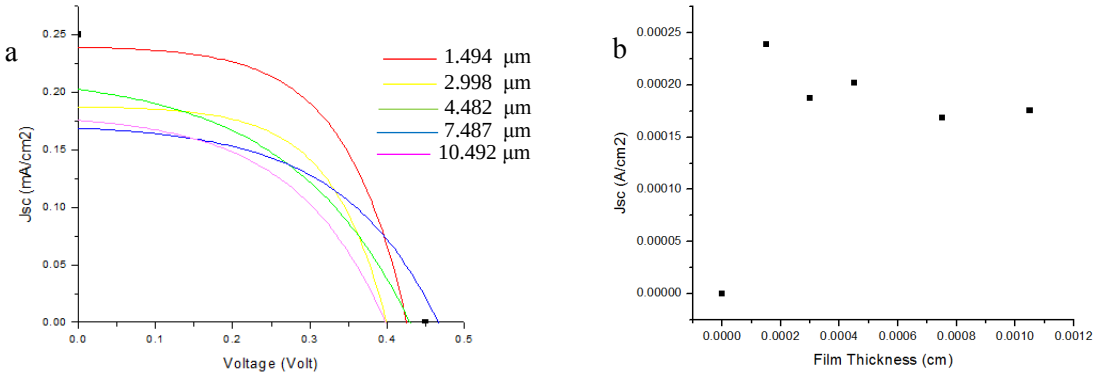

Figure 2. The *I-V* data of five DSSC samples with different thickness (a) and the plot of J_{sc} versus film thickness data with equation 16 graph (b).

Table 2. The input of cell parameters value.

Parameter symbol	Parameter description	Parameter value	Source
e	The electron charge	1.60218×10^{-19} C	-
$\phi_o(\lambda)$	The incident photon flux	1.0×10^{17} cm^{-2} s^{-1}	[22]
L_e	The electron diffusion length	1×10^{-3} cm	[13]
α	The absorption coefficient	5000 cm^{-1}	[13], [23]

Table 3. The cell parameters value after fitting process

Parameter	Ref.	Ref.	Ref.	TiO_2/β-Carotene Dye	Description
e	1.60218×10^{-19} C	1.60218×10^{-19} C	1.60218×10^{-19} C	1.60218×10^{-19} C	Constant
$\phi_o(\lambda)$	1.1369×10^{17} cm^{-2} s^{-1}	1×10^{17} cm^{-2} s^{-1}	0.7×10^{17} cm^{-2} s^{-1}	0.6×10^{16} cm^{-2} s^{-1}	Fitted
L_e	1.5×10^{-3} cm	5.79×10^{-3} cm	1.83×10^{-3} cm	7×10^{-5} cm	Fitted
α	1999.84138 cm^{-1}	1129.89018 cm^{-1}	289.74294 cm^{-1}	3627.04462 cm^{-1}	Fitted
χ^2	2.7296×10^{-7}	4.1116×10^{-7}	4.7175×10^{-8}	5.9549E-10	
R^2	0.94513	0.98509	0.96157	0.9141	

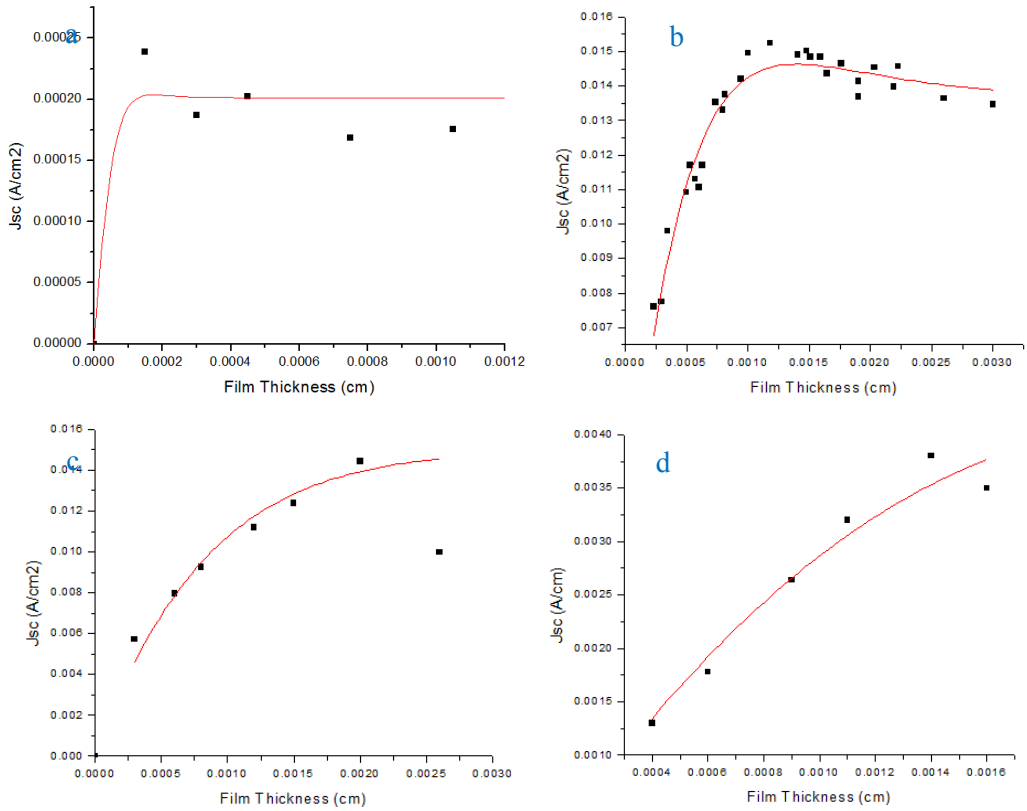

Figure 3. The data plot J_{sc} versus film thickness data with the theoretical modeling fitting results of β-Carotene Dye based DSSC (a), Ref. [19] (b), Ref. [20] (c) and Ref. [21] (d)

Based on Table 3, it was found that equation (16) mathematically has good agreement with each data plot in figure 3a, 3b, 3c and 3d due to their R^2 values which was in the range 0.9141-0.98509. However, except for Figure 3b which was use SnO_2 not TiO_2 as the semiconductor film material, the difference between the fitting results parameters values in figure 3a, 3c and 3d were too far from the initial parameters input values. This was because Figure 3a, 3c and 3d has limited data plot. From the plot of equation (16) which was the same as the figure 3b fitting curve, we found that there were two range of J_{sc}-d data plot. The first range was the zero to optimum film thickness where the J_{sc} rapidly increased with the increased of film thickness, while the second range was the range after the optimum film thickness where the J_{sc} slowly decreased with the increased of film thickness. We found that for Figure 3a, all of the data plot were in the second range, while for Figure 3c and 3d almost all of the data plot were in the first range. That's why we can't got proper fitting results of the parameters values in figure 3a, 3c and 3d data plot. Therefore, this results showed that the diffusion model provided good approximation to describe the dependence of J_{sc} on the film thickness of DSSC. However, in order to properly evaluate the DSSC internal properties such as diffusion length, electron life time and absorption coefficient, proper amount of J_{sc}-d data plot was needed.

5. Conclusion

The J_{sc} of TiO_2/β-Carotene Dye sensitized DSSC strongly depended on the TiO2 film thickness. The J_{sc} was increased rapidly with the increased of film thickness up to 1.494 μm and then decreased slowly as predicted by equation (16). The diffusion model provided good approximation to describe the dependence of J_{sc} on the film thickness of DSSC. However, in order to properly evaluate the DSSC internal properties such as diffusion length, electron life time and absorption coefficient, proper amount of J_{sc}-d data plot was needed.

References

[1] B. O'Regan and M. Grätzel, "A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO_2 Films," *Nature*, vol. 353, no. 6346, pp. 737–740, 1991.

[2] S. Mathew *et al.*, "Dye-Sensitized Solar Cells with 13% Efficiency Achieved Through The Molecular Engineering of Porphyrin Sensitizers," *Nat. Chem.*, vol. 6, no. 3, pp. 242–247, 2014.

[3] J. Gong *et al.*, "Review on Dye-Sensitized Solar Cells (DSSCs): Advanced Techniques and Research Trends," *Renew. Sustain. Energy Rev.*, vol. 68, pp. 234–246, 2017.

[4] B. A. Gregg, "Interfacial Processes in The Dye-Sensitized Solar Cell," *Coord. Chem. Rev.*, vol. 248, no. 13–14, pp. 1215–1224, 2004.

[5] M. Grätzel, "Solar Energy Conversion by Dye-Sensitized Photovoltaic Cells," *Inorg. Chem.*, vol. 44, no. 20, pp. 6841–6851, 2005.

[6] Y. Wang *et al.*, "Density of State Determination of two Types of Intra-Gap Traps in Dye-Sensitized Solar Cells and Its Influence on Device Performance," *Phys Chem Chem Phys*, vol. 16, no. 23, pp. 11626–11632, 2014.

[7] P.-T. Hsiao, Y.-L. Tung, and H. Teng, "Electron Transport Patterns in TiO_2 Nanocrystalline Films of Dye-Sensitized Solar Cells," *J. Phys. Chem. C*, vol. 114, no. 14, pp. 6762–6769, 2010.

[8] J. Villanueva-Cab *et al.*, "Trap-Free Transport in Ordered and Disordered TiO_2 Nanostructures," *Nano Lett.*, vol. 14, no. 5, pp. 2305–2309, 2014.

[9] R. Yang *et al.*, "Fabrication of TiO_2 Hollow Microspheres Assembly from Nanosheets (TiO_2-HMSs-NSs) with Enhanced Photoelectric Conversion Efficiency in DSSCs and Photocatalytic Activity," *Appl. Catal. B Environ.*, vol. 210, pp. 184–193, 2017.

[10] S. A. Kazmi *et al.*, "Electrical and Optical Properties of Graphene-TiO_2 Nanocomposite and Its Applications in Dye Sensitized Solar Cells (DSSC)," *J. Alloys Compd.*, vol. 691, pp. 659–665, 2017.

[11] S. Kundu *et al.*, "Enhancing the Efficiency of DSSCs by the Modification of TiO_2 Photoanodes using N, F, and S, co-doped Graphene Quantum Dots," *Electrochimica Acta*, vol. 242, pp. 337–343, 2017.

[12] S. Soedergren *et al.*, "Theoretical Models for The Action Spectrum and The Current-Voltage Characteristics of Microporous Semiconductor Films in Photoelectrochemical Cells," *J. Phys. Chem.*, vol. 98, no. 21, pp. 5552–5556, 1994.

[13] R. Gomez and P. Salvador, "Photovoltage Dependence on Film Thickness and Type of Illumination in Nanoporous Thin Film Electrodes According to A Simple Diffusion Model," *Sol. Energy Mater. Sol. Cells*, vol. 88, no. 4, pp. 377–388, 2005.
[14] C.-H. Chao *et al.*, "Rapid Thermal Melted TiO_2 Nano-Particles into ZnO Nano-Rod and Its Application for Dye Sensitized Solar Cells," *Thin Solid Films*, vol. 518, no. 24, pp. 7209–7212, 2010.
[15] P. Gu *et al.*, "Influence of Electrolyte Proportion on The Performance of Dye-Sensitized Solar Cells," *AIP Adv.*, vol. 7, no. 10, p. 105219, 2017.
[16] Y. Guo *et al.*, "Preparation of Titanate Nanotube Thin Film Using Hydrothermal Method," *Thin Solid Films*, vol. 516, no. 23, pp. 8363–8371, 2008.
[17] M. C. Kao *et al.*, "The Effects of The Thickness of TiO_2 Films on The Performance of Dye-Sensitized Solar Cells," *Thin Solid Films*, vol. 517, no. 17, pp. 5096–5099, 2009.
[18] M. Ni, M. K. H. Leung, and D. Y. C. Leung, "Theoretical Modelling of The Electrode Thickness Effect on Maximum Power Point of Dye-Sensitized Solar Cell," *Can. J. Chem. Eng.*, vol. 86, no. 1, pp. 35–42, 2008.
[19] Y. Fukai *et al.*, "Highly Efficient Dye-Sensitized SnO_2 Solar Cells Having Sufficient Electron Diffusion Length," *Electrochem. Commun.*, vol. 9, no. 7, pp. 1439–1443, 2007.
[20] I. Shin *et al.*, "Analysis of TiO_2 Thickness Effect on Characteristic of A Dye-Sensitized Solar Cell by Using Electrochemical Impedance Spectroscopy," *Curr. Appl. Phys.*, vol. 10, no. 3, pp. S422–S424, 2010.
[21] M. Hamadanian *et al.*, "The Effect of The Thickness of Nanoporous TiO_2 Film on The Performance of Nanocrystalline Dye-Sensitized Solar Cell," in *5th Symposium on Advances in Science and Technology*, 2011.
[22] K. Zouhri *et al.*, "Numerical Method of The TiO_2 Porosity Effect on Dye Sensitized Solar Cell Energy Efficiency," *Sol. Energy*, vol. 155, pp. 920–933, 2017.
[23] J.-J. Lee, G. M. Coia, and N. S. Lewis, "Current Density Versus Potential Characteristics of Dye-Sensitized Nanostructured Semiconductor Photoelectrodes," *J. Phys. Chem. B*, vol. 108, no. 17, pp. 5269–5281, 2004.