

TiO₂ as the Economically Semi Conducting Layer for Dye-Sensitized Solar Cell (DSSC) Application

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Abstract

Dye-sensitized solar cells are considered a highly promising alternative method for generating electrical power. The DSSC is a photoelectrochemical device designed to efficiently convert solar energy into electrical energy. Titanium dioxide (TiO₂) is the most suitable semiconductor oxide for use in DSSC due to its low-cost materials, easy manufacturing, lack of toxicity, and biocompatibility. Titanium dioxide, or TiO₂, is a highly promising substance utilised in the application of dye-sensitized solar cells as semi conducting layers. The preparation of TiO₂ nanoparticles obtained from using sol-gel method. This paper is to study the effect of the thickness of the semi conducting layer on the performance of the DSSC application. The electrical properties show that the current for 1 layer is the highest among others different thickness. It happens because shorter diffusion routes in thinner TiO₂ layers can help electrons move quicker through the semiconductor material and thinner TiO₂ layers lower the distance required for photogenerated electrons to get to the conductive substrate. From the result of UV-Vis, the absorption coefficient rises when the transmittance falls, and more light is absorbed as a result. A higher absorption coefficient is connected with more light absorption. The bandgap, as determined by the Tauc plot, determines the material's capacity to absorb light at specific energy levels, which contributes to its usefulness in DSSC applications. The XRD pattern shows that the TiO₂ 5 layer has the highest crystallinity and TiO₂ paste from 2 layer until 5 layer is anatase phase.

Keywords: Dye-Sensitized Solar Cell, Titanium Dioxide (TiO₂), Semi Conducting Layer, Sol-Gel Method.

Introduction

In recent years, a multitude of solar cell technologies have been created to efficiently convert sunlight into electrical energy through the process of imitating photosynthesis. The third-generation solar cell which is dye sensitized solar cell (DSSC) is an environmentally friendly technology that is emerging in the field of solar cell-based technology (Agarwal et al., 2021). The DSSC is a photoelectrochemical device designed to efficiently convert solar energy into

electrical energy (Mary, 2014). DSSC was developed by O' Regan and Grätzel in 1991 (Tanihaha, 2010).

The evolution of DSSCs over the past few decades has been marked by significant breakthroughs in materials science, nanotechnology and photoelectrochemical processes (Cai & Qi, 2015). Early difficulties, including effective light absorption and charge separation, prompted advancements in dye design, semiconductor materials, and electrolyte compositions. As a result, DSSCs have progressed from promising prototypes to competitive players in the renewable energy environment. DSSCs can be assembled for a third of the cost of typical silicon-based solar cells through a simple manufacturing technique (Kazim & Nwauzor, 2020).

Photoanode was a vital part to achieve a high conversion efficiency in dye sensitized solar cell. Tuning and modifying this part will stimulate the efficiency of the DSSC device. It was agreed that in order to achieve good efficiency at photoelectrode for DSSC, the layer should feature highlight harvesting, high surface area, fast electron transport and low electron recombination (Zainol & Mamat, 2017).

Titanium dioxide (TiO₂) is an n-type semiconductor (Nadzirah & Hashim, 2013). The naturally occurring oxide of titanium is called titanium dioxide (TiO₂), occasionally referred to as titanium oxide, titanium IV oxide, or titania. This adaptable transition-metal oxide finds utility in a range of current and foreseeable fields, including catalysis, electronics, photonics, sensing, medicine, and controlled drug release (Theivasanthi & Alagar, 2013). Titanium dioxide, TiO₂, has received much research due to its applicability in a variety of fields such as photocatalysts, photovoltaics, sensors, biomaterials, environmental pollutant degradation, optical devices, and supercapacitors. Titanium dioxide, or TiO₂, is a highly promising substance utilised in the application of dye-sensitized solar cells (Ekar et al., 2017). The selection and preparation of the semiconducting layer is critical to the performance of DSSCs, with titanium dioxide (TiO₂) standing out as a main contender due to its beneficial features.

Structural and electrical characteristics of TiO₂ are largely determined by the synthesis process used to create it, which has a direct impact on the solar cell's overall performance. Due to its adaptability and capacity to provide materials with high purity, the sol-gel technique has become more popular in the synthesis of TiO₂ for use in DSSC applications. The demand for energy is increasing in the current day, leading to the development of various energy resources. Therefore, there is an urgent need for research into the creation of inventive energy resources to meet the energy demand of the transformed global community. Renewable energy sources are abundant, environmentally favourable and virtually inexhaustible. And sun among one of renewable sources of energy which emits an immense quantity of energy at no cost. As the emphasis shifts towards optimising DSSC performance, the thickness of the TiO₂ semiconducting layer becomes an important component determining total device efficiency and stability. An option for precise control over the semiconducting layer's characteristics is the sol-gel production of TiO₂. However, the impact of varying TiO₂ layer thicknesses on DSSC performance is still being investigated.

This study intends to explore the impact of TiO₂ as the semiconducting layer synthesised by the sol-gel process in DSSC applications considering these factors. We aim to gain insights into how changes in the synthesis conditions might be used to improve the

stability and efficiency of DSSCs by systematically investigating the sol-gel synthesis process and its effects on TiO₂ characteristics.

In this present work, the impact of varying thicknesses of this semi conducting layer becomes the main focus. An essential tool for measuring electrical behaviour and performance of a solar cell is the current-voltage (I-V) characteristic. It determines the resistance and conductivity of the semi conducting layer. TiO₂-semiconducting layer optical characteristics are characterised using UV-Vis spectroscopy. UV-Vis spectroscopy yields absorption spectra that are essential for understanding the bandgap, light absorption efficiency, and electronic transitions that occur in the material. While, Understanding the structural properties of the TiO₂-semiconducting layer created using the sol-gel process is mostly dependent on X-ray diffraction. Crystal phases can be identified using XRD by examining the diffraction patterns.

It is necessary to facilitate the movement of electrons to generate the electricity (Zainol & Mamat, 2017). This movement is primarily determined by five key components within the DSSC, one of which are the semiconductor layer (Swathi et al., 2018), electrolyte (Ali & Alwan, 2018), dye sensitized, catalyst and conducting substrate. Light is absorbed by a sensitizer attached to the surface of a nanocrystalline semiconductor in DSSCs. There are a few unique advantages of DSSCs such as high energy conversion efficiency, coupled with comparatively low cost, minimal handling expenditures, mechanical durability and light weight. The process happens after light is absorbed, an electron from the excited state of the dye molecule is transferred to the TiO₂ semiconductor layer. Electrons are injected and then travel through a nano crystalline semiconductor, ultimately generating electric current in the external circuit. The generation of this electron is dependent on the electrolyte used, typically the I-/I³⁺- Redox couple. Figure 1 shows the structure of dye-sensitized solar cell (DSSC).

The photosensitizer is a crucial element of a comprehensive DSSC that necessitates careful consideration and attention to enhance the overall conversion efficiency of the cell. The dye molecule's light absorption characteristics and its bonding to the semiconductor surface directly impact the overall efficiency of the cell's conversion process. Titanium dioxide (TiO₂) is extensively researched due to its several potential applications, namely its photocatalytic properties. Titanium dioxide (TiO₂) is the most suitable semiconductor oxide for use in DSSC due to its low-cost materials, easy manufacturing, lack of toxicity, and biocompatibility. The anatase TiO₂ phase in DSSC is anticipated to exhibit strong photovoltaic performance due to its active surface chemistry, high electron mobility, and big band gap energy.

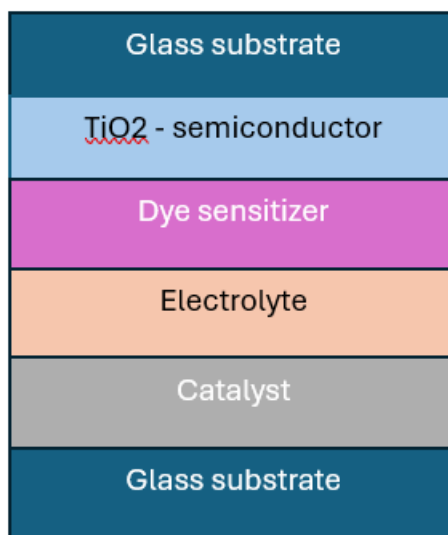


Figure 1. The structure of dye-sensitized solar cell (DSSC).

Although DSSCs have great potential, there are obstacles in the way of their widespread commercialization. Research is still ongoing on topics like improving electron transport efficiency, improving light absorption, and optimising the TiO₂ semiconducting layer. An important factor to consider is the particular synthesis process used for TiO₂, which affects the semiconductor's shape, porosity, and crystallinity, all of which have an impact on the DSSC's overall performance.

Objectives

1. To optimize the synthesis and deposition techniques of TiO₂ for DSSC applications.
2. To investigate the effects of doping and surface modifications on TiO₂ performance.

Experimental Procedures

This section will explain details on the methods and flowchart of this project. Figure 2 shows the flowchart of this experiment.

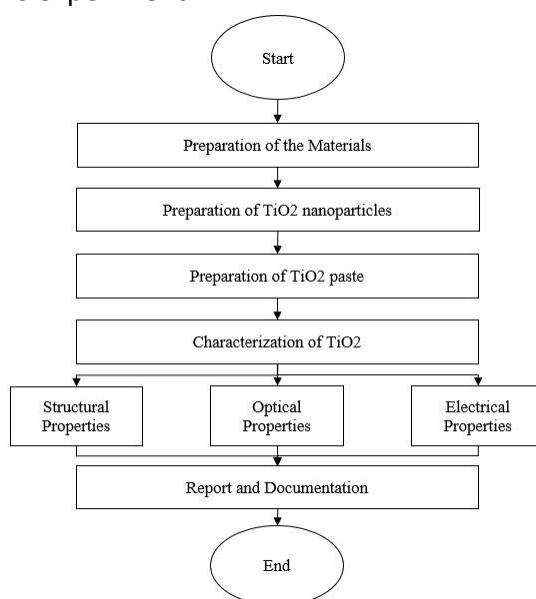


Figure 2. Flowchart of the experiment.

Preparation of Material

A few pieces of equipment that will be used in the projects are beakers, measuring cylinders and petri dishes, along with several types of solutions such as acetone, 200 ml of ethanol, 200 ml of titanium (iv) butoxide and distilled water. Other materials were aluminium foil and filter paper.

Preparation of TiO₂ Nanoparticles

Firstly, the beakers and measuring cylinders would be cleaned by using acetone and distilled water, then put it inside the ultra-sonic cleaner. A diluted solution would be made for hydrochloric acid (HCl). 200 ml of titanium (iv) butoxide was dissolved in 200 ml of ethanol and stirred through a magnetic stirrer. The pH of the solution must be adjusted. The solution has been kept in the dark in aluminium foil for 24 hours. Then, the filter paper would be used to filter the solution. The residue of the solution has been put in the oven for 12 hours at 100°C. After that, the powder would be put in a petri dish and kept in the dark. The powder was milled until it became a fine powder by using a ball mill. The sieve was used to filter the fine powder. Then, the fine powder would be put in a petri dish wrapped with aluminium foil and kept in the dark. The wrapped petri dish has been kept in the desiccator.

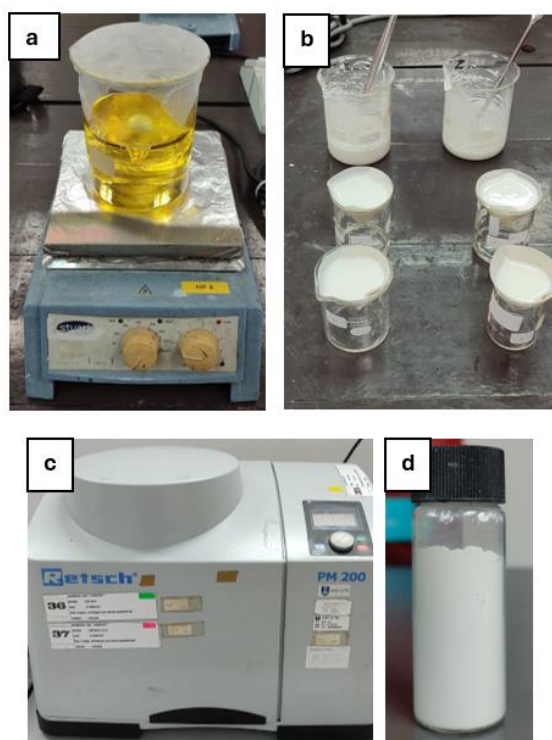


Figure 3. (a), (b) and (c) show the step of the experiment. (d) shows the nanoparticles of TiO₂.

Preparation of TiO₂ Paste

1 gram of TiO₂ powder was added to 50 ml of ethanol and stirred for 30 minutes with a magnetic stirrer until a homogenous paste was obtained. Then, the paste will be placed in the dark and at the same time, the transparent glass sheet will be cut into smaller sizes. The glass was cleaned up by using ethanol and placed inside an ultra-sonic cleaner for 15 minutes. Next, the glass must be completely dried and put inside the spin coat, and then the vacuum

button must be pushed to start the spin coat. After that, 10 drops of the TiO₂ paste will be added to the glass in 1 minute. The glass was put in a furnace at 100°C for 10 minutes and the glass was let rest for 5 minutes before the first layer of coating glass was kept in the container. The same procedure has been repeated for the remaining glass. Lastly, all the glass must be put in the furnace at 500°C for 30 minutes rested for 10 minutes then kept in the container.

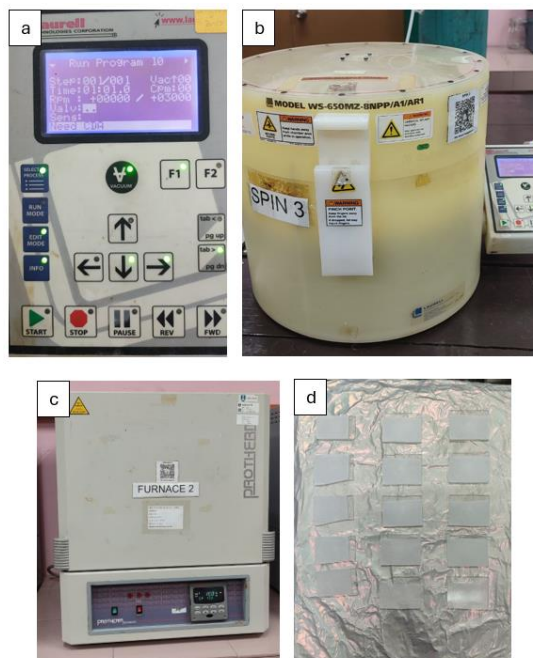


Figure 4 (a), (b), (c) and (d) show the step of the preparation of TiO₂ paste.

Characterization of TiO₂

The result of the project was obtained for three different characterizations of TiO₂ paste and TiO₂ nanoparticles, which are electrical properties Current – Voltage (IV) Characteristic, optical properties UV-Visible (UV-Vis) Spectroscopy and structural properties X-ray Diffraction (XRD). The Current – Voltage (IV) Characteristic was used to find out the electrical connection after using the metal contact process in the project. The formula used in the project as follows:

$$\frac{1}{x} = R \quad (1)$$

Equation 1 is formula to determine R, and x is the slope of the graph.

Other than that, UV-Visible spectroscopy is used to characterize the optical properties of TiO₂. The obtained absorption spectrum could provide information about the band gap energy, which is essential to understanding the semiconducting behavior. The absorption edge in the UV-Vis spectrum can be used for determining TiO₂'s band gap. The Tauc equation (1968) is used to calculate the band gap which is the absorption edge (bandgaps. The formula of Tauc's equation stated at Equation 2:

$$(ahv)^{\gamma} = A(hv - E_g) \quad (2)$$

Where:

α = absorption coefficient using Beer-Lambert Law

h = Plank's constant

ν = frequency of incident photon

A = proportionality constant which is determined by the index of refraction electron and hole effective masses. However, it is usually taken as 1 for amorphous materials.

E_g = the band gap energy

γ = denotes as the nature of the electronic transition.

If the Tauc's equation be compared with the straight-line equation putting the y-axis equal to zero will bring to x-axis. For the energy to be solved, the extrapolation of the linear region of the plot onto the x-axis gives the band gap or edge energy.

Equation 3 is a linear equation:

$$y = m(x) \quad (3)$$

When linear equation equal to zero, then

$$0 = A(h\nu - E_g)$$

Thus,

$$h\nu = E_g \quad (4)$$

Equation 4 represents the energy of photon. Meanwhile, Equation 5 represents the Beer-Lambert Law. It is used to calculate the absorption coefficient.

Beer-Lambert Law

$$I = I_0 e^{-\alpha x} \quad (5)$$

The equation will be arranged and put $x = 1$ which is the thickness of the solution through which the intensity is passing. Then, the standard length of a cuvette will be showed as below:

$$\begin{aligned} \frac{I}{I_0} &= e^{-\alpha x} \\ \log\left(\frac{I}{I_0}\right) &= \log(e^{-\alpha x}) \\ \log\left(\frac{I}{I_0}\right) &= -\alpha x \log(e) \end{aligned}$$

Since the $\log(e) = 0.4343$ and the negative sign is cancelled as the absorbance is equal.

$$\log\left(\frac{I}{I_0}\right) = A = \alpha x (0.4343)$$

The equation be rearranged and put $\gamma = x = 1\text{cm}$,

$$A = \alpha\gamma (0.4343)$$

$$\frac{A}{\gamma} = \alpha(0.4343)$$

$$\alpha = 0.4343A\text{cm}^{-1} \quad (6)$$

The absorbance coefficient formula was stated at Equation 6 which is $0.4343A\text{cm}^{-1}$.

Meanwhile, to determine the bandgap, use the incident energy formula in Equation 7:

$$E = h\nu = \frac{hc}{\lambda} \quad (7)$$

To find the bandgap energy in eV, need to convert Joule to eV which is;

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$$

$$E = \frac{1.986 \times 10^{-25} x (eV m)}{\lambda (m) \times 1.602 \times 10^{-19}}$$

$$E = \frac{1.240 \times 10^{-6} x (eV m)}{\lambda (m)}$$

$$E = \frac{1240 \times 10^{-9} x (eV m)}{\lambda (m)}$$

$$E = \frac{1240 \times (eV 10^{-9} m)}{\lambda (m)}$$

$$E = \frac{1240 \times eV nm}{\lambda (nm)}$$

$$E = \frac{1240}{\lambda} eV$$

(8)

Equation 8 shows the final formula to calculate energy. Band gap energy is the energy needed to excite an electron from the valence band to the conduction band. Lastly, the structural properties can be defined by X-ray Diffraction with the purpose of determining the presence of crystalline and phase composition of the synthesized TiO2.

Results and Discussion

Current – Voltage (IV) Characteristic

Figure 5. show that the Current-Voltage (IV) curve for 5 difference TiO2 layers which are 2.36A for 1 layer, 2.33A for 3 layer and 4 layer, 2.25A for 5 layer, and 2A for 2 layer when the voltage at 10V The resistance value can be calculated from Equation 1. The value of slope can be obtained from Figure 5. The slope for the I-V curve is 1.60586 x 10-10. As shown at Table I The resistance can be obtained from Equation 1 which is 0.6227Ω. Figure 5 show that TiO2 layer have higher current when the coating of TiO2 is 1 layer.

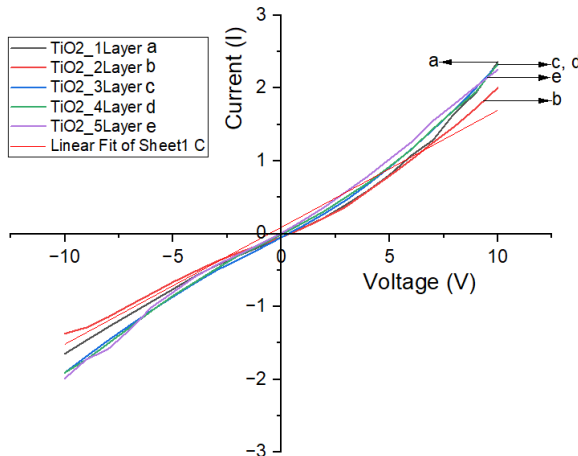


Figure 5. Graph of I-V curve.

Table 1

Results of slope and resistance.

Slope	1.60586 x 10 ⁻¹⁰
Resistance	0.6227 Ω

UV-Visible (UV-Vis) Spectroscopy Analysis

UV-Vis measurements were performed using Optical Spectrometer Jasco/V-670 EX. The result of measurement of transmittance value is shown in Figure 6 where 1 layer is the higher reading compared to another different layer of TiO₂. The ideal thickness of the TiO₂ layer is found to depend on the particle sizes of the TiO₂ layer in order to achieve maximum efficiency. As the particle sizes of TiO₂ layers increase, the ideal thickness of TiO₂ decreases because of intense light back-scattering. Increasing the thickness of TiO₂ layers will lead to a reduction in the amount of light that can pass through the layers, resulting in a fall in transmittance and a consequent decrease in the intensity of incident light reaching the dyes. Furthermore, the charge transfer resistance exhibits an upward trend as the thickness of the TiO₂ layers increases (Jeng et al., 2013).

Figure 6 and figure 7 shows the optical transmittance and optical absorption coefficient spectra for 1 layer, 2 layers, 3 layers, 4 layers and 5 layers in the wavelength range 300-800nm. From Figure 7, the value of absorption coefficient of 5 layers is the highest followed by 4 layers, 3 layers, 2 layers and 1 layer. The relationship between transmittance and absorption coefficient can be concluded from graph in Figure 6 and 7. As the transmittance decreases which resulting in more light is absorbed, the absorption coefficient increases. Increased light absorption is correlated with a higher absorption coefficient.

The absorption coefficient provides information on the absorption edge, which helps determine the optical bandgap using the Tauc plot. The slope of the Tauc figure represents the absorption coefficient, whereas the intercept indicates the bandgap. The bandgap for 1 layer is 1.55eV, 2 layers is 1.54eV, 3 layers is 1.63eV, 4 layers is 1.64 eV and 5 layers is 1.57eV are shown in Figure 8. Higher transmittance means reduced absorption, which is shown in the Tauc plot as a less prominent absorption edge. The energy needed for electrons to migrate from the valence band to the conduction band is correlated with long wavelength absorption of light in a semiconductor material (Lallo et al., 2022).

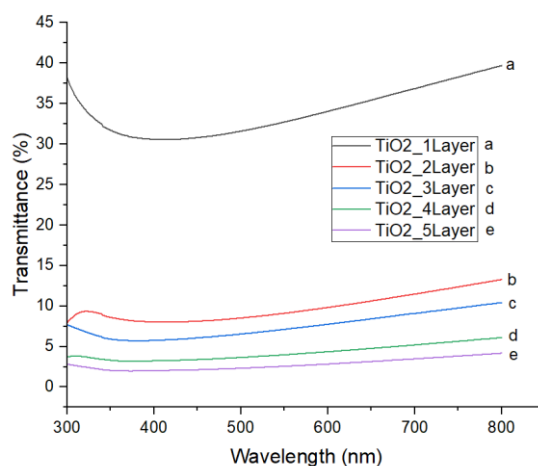


Figure 6. Graph of optical transmittance.

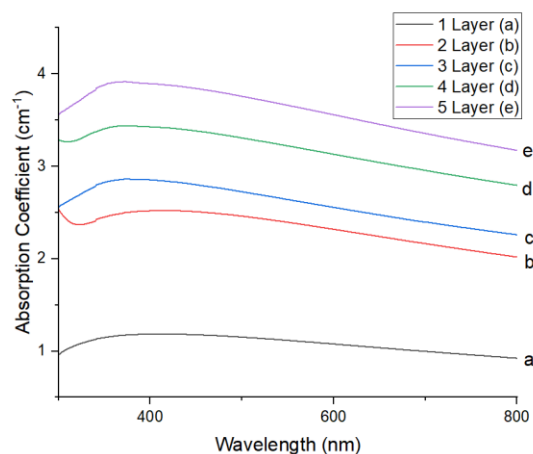


Figure 7. Graph of optical absorption coefficient.

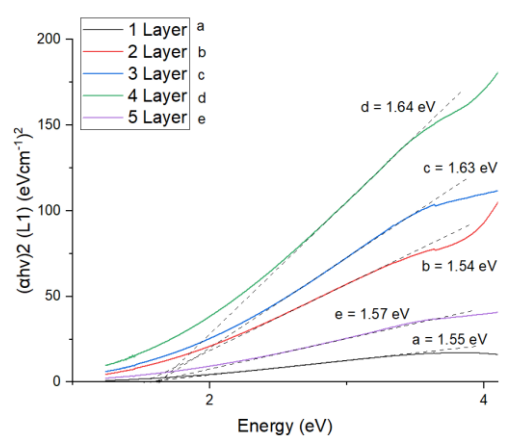


Figure 8. Tauc plot of difference layer of TiO₂, (a) 1 layer, (b) 2 layers, (c) 3 layers, (d) 4 layers and (e) 5 layers.

XRD Analysis

The X-ray diffraction (XRD) pattern of the synthesized Titanium dioxide (TiO₂) nanoparticles is shown in Figure 9. The XRD pattern was obtained using Rigaku Rigaku Ultima IV X-ray Diffractometer. The crystallinity can be observed, it gives up the anatase phase at the peak of 27.24°. Figure 10 show XRD samples consisting of TiO₂ pastes calcined at 500°C. Figure 10 displays the results of the XRD characterization as a diffraction pattern (diffractogram) made up of the distinctive peaks of TiO₂. There is potential peak at 2θ which is 24.64° for 1 layer, peaks at 2θ which is 25.78° for 2 layer, peaks at 2θ which is 25.64° for 3 layer, peaks at 2θ which is 25.4° for 4 layer and lastly peaks at 2θ which is 25.38° for 5 layer referring to the Figure 10. The 1 layer of TiO₂ is amorphous phase (Cabezuelo et al., 2023) while another samples are anatase phase (Wu et al., 2019). The experiment XRD pattern of TiO₂ paste agrees with the JCPDS card no. 01-071-1168. The 5 layers of TiO₂ have more crystallinity than another sample because it has the highest intensity. This is because the intensity of diffraction is greatly influenced by the thickness of the film. In addition, the addition of more layers resulted in a modest decrease in the overall width of the integral, leading to an increase in the size of the crystallite (Elshimy et al., 2020).

Research has revealed that when the thickness of the TiO₂ layer increased, the crystalline size increased while the lattice tension reduced (Elsaeedy et al., 2021) Titania

exhibits three distinct crystalline phases: rutile, which has a tetragonal structure, anatase, also with a tetragonal structure, and brookite, which has an orthorhombic structure. Typically, the anatase form of TiO₂ is favored due to its elevated photocatalytic activity, which stems from its more negative conduction band edge potential, indicating a larger potential energy for photogenerated electrons.

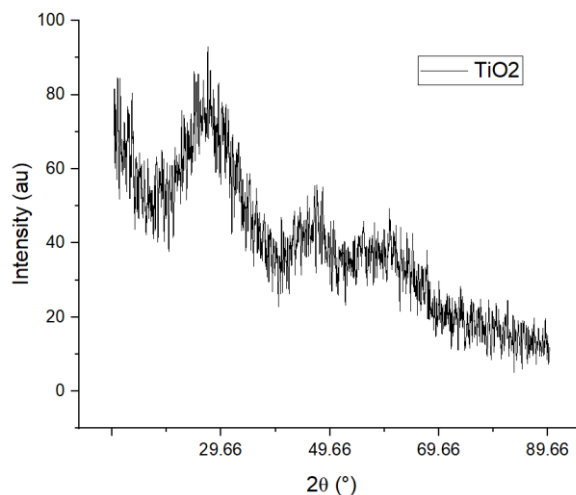


Figure 9. XRD pattern for TiO₂ nanoparticles.

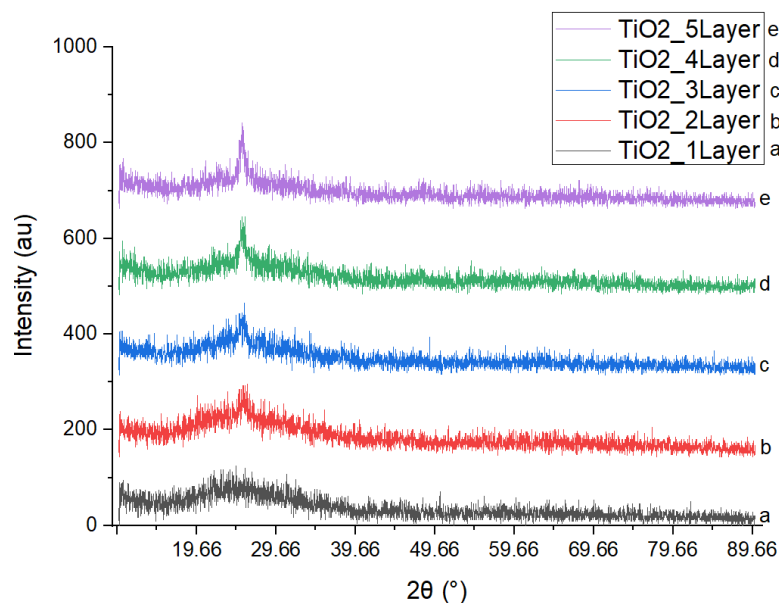


Figure 10. XRD pattern for TiO₂ at different layer.

Conclusion

This research shows that the thickness of the semiconducting layer will have an effect towards the performance of DSSC application. The IV characteristic curves demonstrated a clear relationship of electrical performance on the thickness of the TiO₂ semiconductor layer. I-V curve shows thinner TiO₂ films had higher current densities. While UV-Vis spectroscopy results gave vital insights into the optical characteristics of TiO₂ coatings, which confirmed that thicker layers allowed for more light absorption. XRD analysis revealed the presence of crystalline material of TiO₂ layers. The grain size exhibits a positive correlation with the film's thickness while the lattice strain demonstrates a negative correlation[17]. The result of this

experiment indicates that the important role of TiO₂ thickness influences the intensity of the XRD pattern and the performance of electrical in DSSC.

Contribution

The study on titanium dioxide (TiO₂) as a cost-effective semiconducting layer for dye-sensitized solar cells (DSSCs) provides a diverse contribution to the progress of renewable energy technology. This study aims to improve the performance and cost-effectiveness of DSSCs by utilising the advantageous characteristics of TiO₂, including its high refractive index, broad bandgap, superior chemical stability, and abundance. A notable achievement is the advancement of techniques for enhancing the morphology and crystalline structure of TiO₂, which are essential for enhancing the absorption of light and facilitating electron transport in solar cells. In addition, the research investigates the potential of utilising different doping agents and surface changes to further improve the photocatalytic and photovoltaic efficiencies of titanium dioxide (TiO₂)-based dye-sensitized solar cells (DSSCs). This effort intends to enhance the accessibility of DSSCs for large-scale applications by prioritising scalable and cost-effective production techniques, such as screen printing and doctor-blading. Moreover, the study focusses on the environmental consequences and long-term viability of solar cell materials, highlighting TiO₂ as a more environmentally friendly substitute for the potentially harmful or scarce elements employed in alternative solar cell technologies. In summary, this study adds to the larger objective of promoting the development of clean energy technologies by offering valuable insights into the utilisation of TiO₂ for the creation of efficient, cost-effective, and sustainable DSSCs. This has the potential to promote the broader acceptance and use of solar energy, thereby decreasing dependence on fossil fuels and making a positive contribution to global initiatives aimed at addressing climate change.

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