Dye and activated carbon from *Canarium ovatum* Engl. as photosensitizer and counter electrode for Titania-based dye sensitized solar cell

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Abstract. Natural dye from exocarp and activated carbon from charred shells of *Canarium ovatum* Engl nut was used in the fabrication of dye sensitized solar cell (DSSC). Anatase titania (titanium dioxide, TiO₂) nanoparticles was used as semiconducting layer deposited on a transparent conductive indium tin oxide glass using doctor blade method. TiO₂ film thickness and soaking time in dye were varied to show response in terms of fill factor (FF), short circuit current density (J_sc), open circuit photovoltage (V_oc), and conversion efficiency (η). In a 2.0 cm² active surface area tested under solar irradiance, assembled DSSC at optimum conditions garnered 0.768 desirability with FF, J_sc, V_oc and η values of 0.601, 6.293 mA/cm², 0.446 V, and 1.792, respectively.

1. Introduction

The rise of innovation and technology had taken a toll on the world’s depleting source of fossil fuels. This energy crisis has been caused by overconsumption, inefficient use of energy, overpopulation, and failure to explore and make use of renewable sources. Although efforts had been made by the government and concerned parties, the energy crisis is on-going and is getting worse. Humanity’s hope to reduce its dependence on non-renewable energy, such as fossil fuels, is to rely towards renewable sources. Among renewable sources that are currently being used, solar energy poses the greatest potential as major energy source for the future. Not only it is abundant in any part of the globe in certain periods, with total of 3,850,000 exajoules (EJ) of energy absorbed by the Earth annually, solar energy is clean and is non-detrimental for the environment. 2000 World Energy Assessment stated that the solar energy’s potential is about 1,575 to 49,837 EJ annually. This digit is folds larger than the world final energy consumption in 2015 that was about 393 EJ [1]. Solar energy is the energy from the sun that is changed over into heat or electrical energy. This energy is considered to be the cleanest and most plenteous renewable energy source available. This type of energy source also possess flexibility in generation since it can be sourced from either a central station solar power plant, or from individual houses and establishments through solar panels [2]. The International Energy Agency (IEA) reported in 2011 that the advancement of this type or renewable energy offers huge benefits in the long run. It strengthens countries’ energy security by providing an inexhaustible power source whilst boosting sustainability, reducing pollution, and addressing the ever-increasing fossil fuel energy price. IEA strongly suggests incentivizing early deployment of this type of energy since investments to which provides benefits in a global scale [3].
Solar cell is a type of photoelectric cell, a device whose electrical qualities differ when exposed to light. It has received large attention in the society due to its cheap and clean technology that harnesses solar energy efficiently. To further decrease its production cost, while increasing efficiency and enhancing effectivity, is a big challenge to the solar technology these days. One of the most capable types of solar cells is the dye sensitized solar cells (DSSC). Among different sorts of solar cells, DSSC have pulled in much enthusiasm from individuals. A DSSC is a cheap solar cell having a place with the group of thin film solar cells. It is the most able promising photovoltaic cell that utilizes nanotechnology [4]. DSSC falls under solid/liquid type or third generation of photovoltaics. DSSC differs from other types of solar cells since it does not depend on the principle of traditional p-n junction for its operation where common solid-state solar cells like those based on crystalline or amorphous silicon depends on. It is also classified as photoelectrochemical solar cell since it utilizes photons, charges and electrolytes. DSSC uses transparent conducting oxide or transparent conductive glass, electrodes, semiconductor, electrolytes and sensitizer for its basic operation. The change of solar energy to electric flow depends on charge division. This type of solar cells has drawn people’s interest because of its low-priced fabrication cost and reasonable high efficiency beyond 11% at full sunlight [5]. Normally, DSSC uses platinum to catalyse the iodine redox couple and complete the electric circuit. This element is a good catalytic material in preparation of counter electrodes; however, it is rather costly. Choices to supplant platinum have been analysed, and one of these is carbon-based material. A DSSC using carbon as counter electrode, achieved 6.72% of the maximum power conversion efficiency with an area of 0.25 cm². This value is comparable to 8.19% maximum power conversion efficiency of the cell using conventional platinum at the same experimental conditions [6].

The Bicol Region, specifically at Partido Area, provides abundance in Canarium ovatum Engl, locally known as Pili. This fruit bearing tree is endemic to the region and its fruit is a source of food for the locals. However, parts of this fruit – particularly the skin or the exocarp, and the shell is often discarded and thrown away. Its skin, when already ripe, shows a characteristic purplish black appearance making it a good source of dye. Then again, its shell can be utilized as activated carbon [7] and its prevalent smaller scale – pores give it a tight structure, great mechanical quality, hardness, and protection from whittling down or wearing by friction. Successful and ongoing studies and researches on converting solar energy to electrical energy using DSSC has motivated the researcher to carry out the study of fabricating a DSSC using Canarium ovatum Engl exocarp dye as dye and activated carbon produced from its shell as counter electrode. The use of this dye and counter electrode is promising because of its economical aspect and environmental feature since it is single sourced and organic.

2. Methodology

2.1. Preparation of dye from Canarium ovatum Engl. exocarp
Fruits of Canarium ovatum Engl. tree were obtained from local farmers in Lagonoy, Camarines Sur. The fruits were selected based on its maturity as determined by the colour of its exocarp which is dark purple to black when fully ripe. Fruits with no physical damage were carefully selected, washed under running water, and allowed to dry at room temperature [8]. The fruits were then submerged in 90°C water for 15 min. Exocarps were collected by manual peeling, were air dried for 3 d, and were ground using a food blender. Approximately 150 g of the ground samples were completely submerged in 300 mL absolute ethanol for 24 h with constant stirring. The mixture was then filtered through a Whatman filter paper. Collected natural dye was stored in glass bottles.

2.2. Preparation of activated carbon from Canarium ovatum Engl. shell
Shells left from previous procedure were washed to remove adhering pulp and were allowed to dry at room temperature. After removal of testa and kernel, the shells were crushed and were readied for carbonization. Carbonization was carried out at 400°C in a closed steel vessel that is placed in a laboratory furnace (Heraeus UT-6200) for 30 min. Charred material was ground and sieved through a
200-mesh sieve to obtain a fine powder with average particle size of 74 microns. Collected powder were then chemically activated using NaOH in a 8:1 carbon:OH- weight ratio [9].

2.3. TiO\textsubscript{2} paste preparation and application
Titania paste was prepared by admixing 2 g of anatase TiO\textsubscript{2} nanoparticles, 6 mL of 99.5 w/w% acetic acid, and 0.5 mL of Triton X100 as surfactant. The mixture was stirred for 20 mins. Afterwards, 12 mL of 99.8 w/w% ethanol was slowly added whilst continuously stirring for another 20 mins [10]. The paste was then applied unto the ITO (indium tin oxide) conductive glass using doctor blade method at variable thickness (30 µm, 60 µm, 90 µm) at a surface area of 2.0 cm\textsuperscript{2}.

2.4. Preparation of anode and counter electrode
For anode, prepared TiO\textsubscript{2} layered ITO conductive glass was heated to 100\textdegree{}C on a hot plate to remove remaining moisture on the layer. It was then allowed to cool under room temperature. Afterwards it was soaked in the dye for adsorption at room temperature at variable time (12 h, 18 h, 24 h). For counter electrode, 2 g of prepared activated carbon were mixed with 12 mL of 99.8 w/w% ethanol for 15 mins. The mixture was applied unto another ITO conductive glass using doctor blade method at 30 µm at a surface area of 2.0 cm\textsuperscript{2}.

2.5. Preparation of electrolyte solution
The electrolyte solution was made by mixing 0.125 g of iodine and 0.85 g of potassium iodide in 10 mL of acetonitrile.

2.6. Assembly of DSSC
Sealing agent (hot melt adhesive film) was placed on the dye sensitized plate. 2 drops of the electrolyte solution were applied. Afterwards, the counter electrode plate was placed facing the dye sensitized TiO\textsubscript{2}. The sandwiching of the two plates is counterbalanced with the goal that each plate has an uncovered bit for testing. Binder clips were used to fix the two plates together whilst being heated at 50\textdegree{}C for the sealing agent to glue the plates together.

2.7. Test for DSSC
Fabricated DSSC was tested under solar irradiance. Parameters were measured using a multimeter (Bestguard DT-266). The negative clip was attached to the TiO\textsubscript{2} positive dye sensitized plate and the positive clip was attached to the counter electrode plate. The researcher utilized a software operating response surface methodology (RSM) to evaluate the parameters in the study and provide optimization. Also, RSM will be used to further study the interactive effectiveness of film thickness of TiO\textsubscript{2} nanoparticles and soaking time, in hours, to fill factor (FF), open circuit voltage (V\textsubscript{OC}), short circuit current density (J\textsubscript{SC}), and conversion efficiency (\eta).

3. Results and Discussions

3.1. Fabricated DSSC
The design for the fabrication of the DSSC that made use of Canarium ovatum Engl. dye and activated carbon as sensitizer and counter electrode involved a set of different layers of components stacked in serial. This configuration is shown in Figure 1.

3.2. Performance of DSSC
Design-Expert\textsuperscript{®} was used to provide variable conditions of TiO\textsubscript{2} nanoparticles film thickness and soaking time in analysing the performance of the fabricated DSSC. In relation to the second specific objective, the responses that were gathered includes FF, J\textsubscript{SC}, V\textsubscript{OC} and \eta.
3.3. Responses

3.3.1. Fill Factor (FF). RSM suggested mean model for fill factor due to a sequential p-value of <0.0001. Nevertheless, adjusted $R^2$ and predicted $R^2$ of the model equates to zero. This means modelling FF against variable factors is not possible and graphical modelling would yield no response as shown in Figure 2. Nonetheless, not significant lack of fit of the analysis of variance of the mean model of the FF response implies reliable data gathered and modelling of which along with other responses for optimization is fit and acceptable.

3.3.2. Short circuit current density ($J_{SC}$). Evaluating short circuit current density against varying factor values, RSM suggested quadratic modelling of the response. Adjusted $R^2$ and predicted $R^2$ of the model is 0.9005 and 0.6833, respectively. On the other hand, $R^2$ is 0.9503 in fit statistics. The model is considered to be significant considering its F-value of 19.11. Design-Expert notes that there is just a 0.28% possibility that a F-value this huge could happen because of noise. The absence of fit F-value of 5.93 suggests the absence of fit isn't significant comparative with the unadulterated error. There is a 14.78% possibility that a Lack of Fit F-value this enormous could happen because of noise. $J_{SC}$ behaves like a curve in response to variable anode thickness, peaking at 60 µm with actual $J_{SC}$ value of 6.5105 mA/cm². Also, nominal response is noticed against soaking time. Minimal positive inflection is seen towards the 12-hours and 24-hours end. This model is graphically presented in Figure 3.

3.3.3. Open circuit photovoltage ($V_{OC}$). The open circuit photovoltage response was evaluated against factors using response surface methodology. RSM suggests that $V_{OC}$ follows a quadratic model with adjusted $R^2$ and predicted $R^2$ of 0.7843 and 0.0906, respectively. The value of $R^2$ in fit statistics is 0.8921. The Model F-value of 8.27 suggests the model is significant. There is just a 1.84% possibility that a F-value this huge could happen because of noise. P-values under 0.0500 demonstrate model terms are significant. Values more prominent than 0.1000 show the model terms are not significant. The absence of fit F-value of 3.02 infers the absence of fit isn't significant comparative with the unadulterated mistake. There is a 25.84% possibility that an absence of fit F-value this enormous could happen because of noise. Non-significant absence of fit is useful for the model. The model is graphically introduced in Figure 4. Similar to $J_{SC}$, it can be observed that, relevant to anode thickness, $V_{OC}$ behaves in a curve, increasing in value from 30 µm until it reached its peak to a value of 0.458 V and starts decreasing until 90 µm. On the other hand, with respect to the soaking time, there has observed a minimal response, only having a slight positive inflection towards 12-h and 24-h end.

3.3.4. Conversion efficiency ($\eta$). Investigating the response of conversion efficiency against variable factor values, RSM suggests that $\eta$ follows a quadratic model with adjusted $R^2$ and predicted $R^2$ of 0.7502 and 0.4736, respectively. The value of $R^2$ in fit statistics is 0.8751. The Model F-value of 7.00 infers the model is significant. There is just a 2.61% possibility that a F-value this huge could happen because of noise. The absence of fit F-value of 0.53 suggests the absence of fit isn't significant comparative with the unadulterated error. The model is graphically introduced in Figure 5. It can be observed that, relevant to anode thickness, $\eta$ behaves in a curve, increasing in value from 30 µm until it reached its peak to an actual $\eta$ value of 2.40614 and starts decreasing until 90 µm. On the other hand,
with respect to the soaking time, there has observed a minimal response, only having a nominal positive inflection towards 12-h and 24-h end.

**Figure 2.** 3D surface modelling of FF response.

**Figure 3.** 3D surface modelling of J_{SC} response.

**Figure 4.** 3D surface modelling of V_{OC} response.

**Figure 5.** 3D surface modelling of η response.

| Factors                      | Response Values |
|------------------------------|-----------------|
| TiO$_2$ Film Thickness(µm)   |     | V_{OC} (V) | J_{SC} (mA/cm²) | FF | η |
| Soaking Time (hr)            |     |     |     |     |    |
| 55.249                       | 12  | 0.446 | 6.293 | 0.601 | 1.793 |

3.4. Data optimization of DSSC

Design-Expert® provided the data for the optimization of factors from the actual responses from experimental data. Necessary constraints must be set to obtain the optimum value of the TiO$_2$ anode thickness and soaking time to achieve the most desirable FF, J_{SC}, V_{OC} and η responses. Both operating factors are targeted to be at minimal since it is best, in economic consideration, to fabricate DSSC with the least amount of TiO$_2$ and the fastest possible soaking time. All the responses are set to be maximized
since desirability of DSSC is relevant to $V_{OC}$, $J_{SC}$, FF and $\eta$. Both the factors and responses are set to have equal importance. Optimum conditions, considering the constraints given in Table 1.

Conclusion
Utilizing *Canarium ovatum* Engl. exocarp dye as natural sensitizer and activated carbon derived from its shells as counter electrode in the fabrication of dye sensitized solar cell yielded positive result. Varying values of titanium dioxide film thickness and soaking time in dye generated effect in the responses. Short circuit current density, open circuit photovoltage and conversion efficiency have similar reactions to variable operating parameters, that is increasing to a peak and then decreasing in terms of anode thickness and minimal positive inflections towards the end of experimental soaking time. On the other hand, modelling fill factor, as far as this study is concerned, yielded no response. Nevertheless, all the responses have insignificant lack of fit that makes data reliable and modelling for optimization acceptable. Design-Expert® provided optimum conditions to provide the most desirable outcome by minimizing the factors and maximizing the responses. In which, fabricated DSSC operating at 55.249 µm TiO$_2$ anode film thickness and soaked in dye at 12 hours would produce FF of 0.601, $J_{SC}$ of 6.293 mA/cm$^2$, $V_{OC}$ of 0.446 V, and $\eta$ of 1.792.

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