Response Surface Modelling of Titania Photoanode Dye Sensitized Solar Cell (DSSC) Using Central Composite Design.

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Abstract. The purpose of this work is to enhance the performance of photoelectrode element in Dye-Sensitised Solar Cells (DSSC) by using a Response Surface Methodology (RSM) technique. Most of previous work related to photoelectrode enhancement have relied on the traditional method known as One Factor at a Time (OFAT), which has the limitation to evaluate the interaction effect for TiO_2 Thickness and dye molarity and requires an excessive amount of experimental run. To address this issue, RSM is used to optimize the performance of DSSC in studying the relationship between two parameters TiO_2 film thickness and the concentration of N719 dye molarity. The RSM technique also helps in finding the best mathematical model on how these parameters interact and affect the result of Power Conversion Efficiency (PCE). The result from this study shown that these two variables, TiO_2 film thickness at 10 μm and the concentration of N719 at 0.4mM are significant and generated the highest value of PCE at 2.86%, with high coefficient of determination R^2 (0.9983). The R^2 of 0.9983 is close to 1 shows the strong correlation between the variables TiO_2 film thickness and the concentration of N719 dye molarity.

Introduction

Solar technology known as photovoltaic (PV) shows a high demand since many decades ago [1][2]. A dye-sensitive solar cell (DSSC) as third generation solar technology is a composite device with five different elements including a transparent conducting oxide glass (TCO), TiO_2 photoelectrode layer, dye sensitizer, a counter electrode, and an electrolyte [3]. DSSC provided a viable alternative to PV by enhancing the ability of the sensitizer to harvest the light and the transport charge of photoanode [4]. The performance of DSSC is affected by the thickness of TiO_2 photoelectrode. A necessary TiO_2 thickness will allow an efficienct electron diffusion from TiO_2/dye/electrolyte interface and resulting to higher current density. Previous researches has proved that, the best TiO_2 thickness is in the range of 7-30 μm, in absorbing light and the performance start to decrease with increasing of film thickness above 14.5 μm [6]. The concentration of N719 have a significant impact on enhancing the performance of DSSC in absorption of light. The higher concentration of dye N719 lead to the higher optical absorption that enhancing the performance of DSSC in harvesting light[7].

By applying the RSM technique in this research, it helps in determining the main factors and interaction effect between the film thickness and the concentration of N719 that effect the performance of DSSC[8]. There is no study conduct to determine the interaction between both TiO_2 thickness and concentration of N719 towards better PCE. Hence, the reason why this study is conducted. In addition, the RSM technique helps in reducing the number of experiments and time in preparing the number of sample.

Methods

Design of experiment by response surface methodology

Material and technique used in DSSC fabrication is based on reference [9]. RSM is applied to optimise the processes and to understand the connections between the TiO_2 film thickness (A) and the concentration of N719 dye (B) on the fabrication of TiO_2 compact layer. **Table 1** shows the ranges and levels of the variables A and B, and PCE as respond for this experiment. The statistical expert (Design Expert 13, Stat Ease Inc, MN, USA) produced RSM/CCD with two variables and a total of 13 runs of experiments as shown in **Table 2**. The flowchart in **Fig. 1** shown a RSM technique for model validation and PCE optimization. The Design Expert Software was used to predict the best values for each variable in the experiment, with the goal of achieving the maximum PCE. The efficiency of the model can be seen by conducting tests and comparing the experimental data to the predicted result outcomes. The precision of the model was determined using residual standard errors (RSE).

Table 1: Experimental range and level of each independent factor.

Factors	Notation	Unit	Actual		
			Low	Middle	High
TiO_2 film thickness	A	µm	5	10	15
Concentration of N719 dye	B	mM	0.2	0.4	0.6

Table 2: Central Composite Design (CCD) for TiO_2 compact layer using RSM and experimental data.

No. of Run	A: TiO_2 film thickness (µm)	B: Concentration of N719 dye (mM)	PCE (%)	
			Experimental	Predicted
1	5	0.2	1.71	1.74
2	10	0.2	2.71	2.68
3	15	0.4	2.38	2.37
4	10	0.4	2.85	2.86
5	15	0.2	2.01	2.03
6	10	0.4	2.86	2.86
7	10	0.2	2.70	2.68
8	5	0.6	1.43	1.42
9	10	0.4	2.85	2.86
10	15	0.6	2.33	2.31
11	5	0.4	1.80	1.78
12	10	0.6	2.65	2.66
13	10	0.6	2.64	2.66

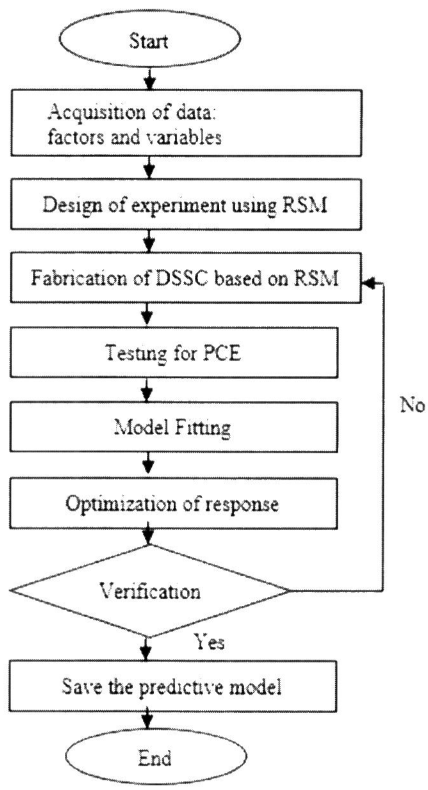

Fig. 1 Response Surface Methodology

Characterization. In this study, current-voltage performance of complete solar cell was obtained under solar simulators at intensity of 1.5 air mass densities (AM1.5). Keithley 4200 source meter was used to measure the output voltages and currents The plotted graph of I-V was then analysed to obtain the fill- factor (FF) and power conversion efficiency (PCE, η).

Result and Discussion

Table 2 shows the predicted result and data from the experiment generated by Design Expert Software. The data was fitted and equation model was created. The significance of the quadratic model for the response variable PCE is indicated by the analysis of variance (ANOVA) in **Table 3**. The F-value of 829.83 indicates that the model is significant. There is only a 0.01% chance that the large F-value could occur due to noise. Model terms with p-values less than 0.05 are considered significant. [10]. In this case A, AB, A^2, B^2 are significant model terms. p-values greater than 0.1000 shows the model terms are insignificant. The insignificant model terms are good as it shows the model is fitted and has excellent predictability and improve the model [11]. The F-value of 37.08 indicates that the lack of fit is significant. A lack of fit F-value generated by noise has a 0.22% chance of occurring.

Table 3: ANOVA for quadratic model for response PCE

Source	Sum of Square	df	Mean Square	F-value	p-value	
Model	2.85	5	0.5693	829.83	<0.0001	significant
A-TiO_2 thickness	0.5281	1	0.5281	769.76	<0.0001	
B-N719 concentration	0.0008	1	0.0008	1.17	0.3160	
AB	0.0900	1	0.0900	131.19	<0.0001	
A^2	1.99	1	1.99	2906.60	<0.0001	
B^2	0.1178	1	0.1178	171.64	<0.0001	
Residual	0.0048	7	0.0007			
Lack of Fit	0.0046	3	0.0015	37.08	0.0022	significant
Pure Error	0.0002	4	0.0000			
Cor Total	2.85	12				

Table 4: ANOVA fit statistic

Std. Dev.	0.0262	**R^2**	0.9983
Mean	2.38	**Adjusted R^2**	0.9971
C.V. %	1.10	**Predicted R^2**	0.9873
Adeq Precision	81.0732		

Table 5: Coefficients in terms of coded factors Anova

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	2.86	1	0.0131	2.83	2.89	
A- TiO_2 thickness	0.2967	1	0.0107	0.2714	0.3220	1.00
B- N719 concentration	-0.0100	1	0.0093	-0.0319	0.0119	1.00
AB	0.1500	1	0.0131	0.1190	0.1810	1.00
A^2	-0.7894	1	0.0146	-0.8240	-0.7548	1.01
B^2	-0.1966	1	0.0150	-0.2320	-0.1611	1.01

As a result, the model has high coefficient of determination with R^2 value 0.9983 as shown in **Table 4**. The R^2 value near to 1 shows the model is considered to have strong regression. The predicted R^2 and adjusted R^2 values are 0.9873 and 0.9971, respectively, indicating an adequate level of agreement between the two variables. The different between this predicted R^2 and adjusted R^2 is less than 0.2. The adequate precision measures the signal-to-noise ratio, which the ratio should be greater than 4. In this scenario, the model's ratio of 81.0732 shows that the signal is adequate. This model can be used to navigate the design space. Furthermore, the model has a low coefficient of variation (CV) and standard deviation (SD), which indicated that the analysis is acceptable [8].

$$PCE = \mathbf{2.86} + \mathbf{0.2967} * \mathbf{A} - \mathbf{0.01} * B + \mathbf{0.15} * AB - \mathbf{0.7894} * A^2 - \mathbf{0.1966} * B^2 \qquad \textbf{(Eq. 1)}$$

The model presented in **Eq. (1)** represents the experimental response and depicts the impact of dependent and independent variables. The results highlight a strong alignment between the quadratic model and the experimental data. The equation enables prediction of the response for various values of each variable. Notably, in the equation, factors with high values are denoted as +1, while those with low values are denoted as -1. The coded equation could be utilized for comparing the factor coefficients to determine the significance of the elements. From the **Eq. (1)**, A is represented the TiO_2 film thickness and B represented the concentration N719 dye. **Table 3** shows a quadratic model with factor of A, AB, A^2, B^2 are significant due to the value p-value less than 0.05 compared to the factor of B, the p-value is 0.316 which is higher than 0.05 makes the factor be insignificant. This factor of B shows that the concentration of N719 that start from range 0.2mM to 0.4mM does not have any mutual influence on this experiment. The significant factor of A, AB, A^2, B^2 form the overall quadratic equation model.

Fig. 2(a) shows the normal probability plot vs. the studentized residual, which produces a straight li ne indicating that errors are normally distributed and an adequate model is formed. From **Fig. 2(b)**,t he studentized vs residual graph shows almost all the data plotted are distributed equally around the mean point of the response variables. Furthermore, this figure demonstrates that the model is good b ecause most of the points fall between the lowest and maximum limits, resulting in no continuous er ror. Only one data fall above the lowest limit, shows that the result still acceptable for the model. Sh own in **Fig. 2(c)**, the graph predicted vs actual represent linear function showing the data have high accuracy proving the model performs well and properly describes the experimental data.

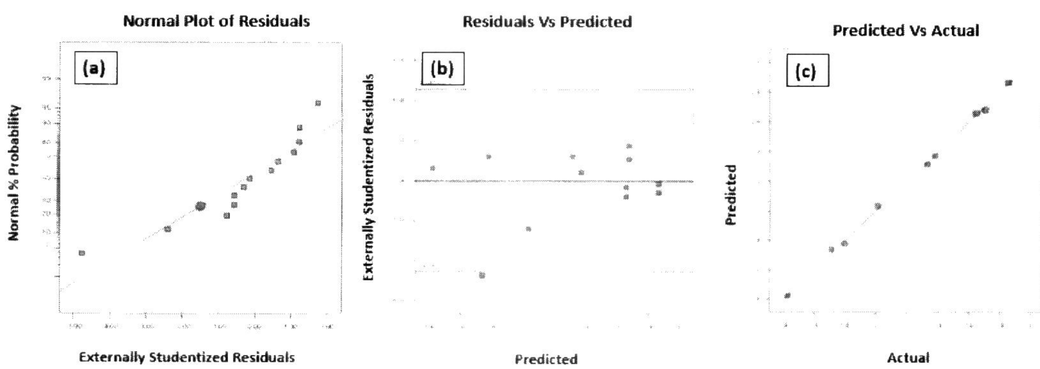

Fig. 2 Plots of (a) normal vs studentized (b) Residual versus predicted and (c) Predicted versus actual.

From **Fig.3 (a)**, the value of PCE increasing with the increasing of the thickness and achieve the p eak when the thickness is 10 μm, then PCE start to fall at thickness film is 13 μm. For N719 conc entration as shown in **Fig.3 (b)**,the result of PCE does not show obvious increment compare to the plot for TiO_2 film thickness. This result proves that the concentration of N719 (B) is insignificant model. **Fig.3 (c)** shown a green line which represents the TiO_2 film thickness (A) while the blue li ne represents the concentration of N719 (B). To investigate the relationship between each factor a nd the surface response, graphs of PCE versus TiO_2 film thickness and the concentration of N719, are presented through **Fig.3 (c)**,. The graph shows that the interaction between these two factors o ccur. The different film thickness and concentration of N719 gives the different value of PCE.

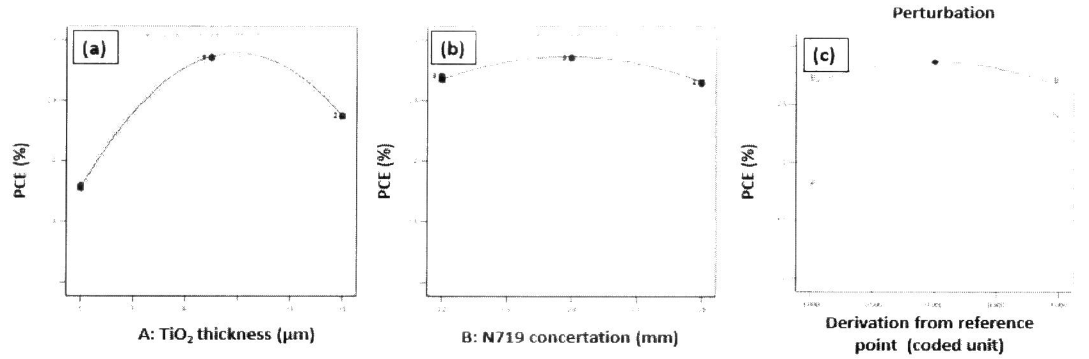

Fig. 3 Plots of (a) PCE (%) vs TiO_2 film thickness (b) PCE (%) vs concentration of N719 and (c) PCE (%) vs TiO_2 film thickness and concentration of N719.

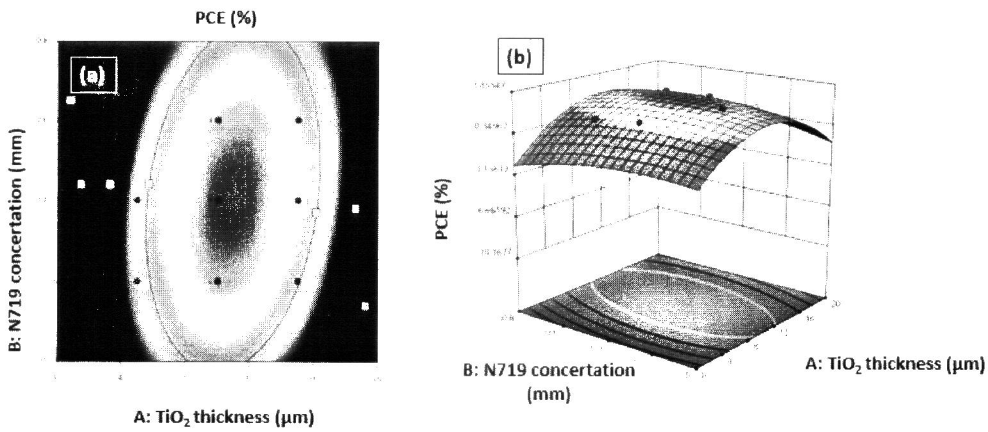

Fig. 4 (a) Two-dimensional (2D) and (b) Three-dimensional (3D) of contour surface PCE with vs TiO_2 film thic kness and N719 concentration

Fig. 4 (a) and **(b)** shows 2D and 3D contour plot of TiO_2 film thickness and N719 concentration a s variable and PCE as the response generated by the RSM. **Fig. 4 (b),** shows the value PCE at 2.8 6% is the highest peak of the curve, this shows there are strong relationship between these two va riables with PCE response. This proves, the factor AB is significant and gives big impact to the re sponse PCE.

Photovoltaic performance of TiO_2 photoelectrode.

Summary

Based on the experiment results, it can be proven that increasing the TiO^2 film thickness and concentration of N719 molarity can increase the PCE of DSSC. The study also prove that the central composite design was effectively used to investigate and figure out the connection between TiO^2 film thickness and concentration of N719 towards the PCE. The maximum PCE was generated at 2.86% when the TiO^2 film thickness and concentration of N719 were at 10 µm and 0.4 mM, respectively.

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