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TiO_2 THICKNESS AND GRAPHENE QUANTUM DOTS VARIATION IN PHOTOANODE OF DYE SENSITIZED SOLAR CELL USING RESPONSE SURFACE METHODOLOGY (RSM) TECHNIQUE.

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ABSTRACT

In this study, the range of TiO_2 thickness and GQDs amount were varied to determine the efficiency response of DSSC by response surface methodology (RSM). The best efficiency of 5.65% obtained when the thickness was optimized at 5 μm and 50 μL GQD amount was spin coated on top of TiO_2 photoanode. This efficiency may be due to GQD absorbed efficiently on TiO_2 surface at 5 μm thicknesses and the photoluminescence behavior by GQD employed in this work. Hence, improved light harvesting in the visible region and generated higher photo current density. A good model for comparing the actual and predicting values of power conversion efficiency of DSSC by varying the TiO_2 thickness and addition of GQD amount were obtained through this work.

Keywords: GQD; RSM; thickness; DSSC

INTRODUCTION

DSSC is a type of photochemical cell, which convert solar to electrical energy in moderate conversion efficiency. DSSC also, offer other advantages such as easy to fabricate and low-light application compare to silicon and thin-film solar cells [1–4]. However, to improve its performance, photoanode element is one crucial part in DSSC, where it consists of dye sensitizer and TiO_2 semiconducting layer. TiO_2 nanomaterials were used widely in photoanode DSSC due to its stability for long-term, wide bandgap, low cost and high photo activity. However, it causes poor absorption on visible-region, lack of charge-carrier transport and electron recombination between TiO_2/dye/electrolyte interfaces which limit electron diffusion and resulting low current density [5–7]. To improve these issues, the incorporation of other nanomaterial known as graphene quantum dots (GQD) into TiO_2 photoanode is essential. GQD is describe as carbon nanoparticles of a semiconducting material with size of 2-10nm. This GQD of zero-dimensional shows excellent properties such as stable photoluminescence, quantum confinement and edge effect, carboxylic group at edge that make it easy to attach with other superconducting material [8-9].

Previous studies used GQD in photoanode have been reported such as composite GQD-TiO_2 can enhance photon current density and efficiency by 30.9% and 19.6% respectively by incorporating GQD compare to pristine TiO_2 photoanode. GQD also used to tune the bandgap energy of semiconducting layer TiO_2 due to quantum confinement effect of GQD. Hence the absorption edge expands to visible region spectrum. A doping of GQD-TiO_2 mixture improved the photocatalytic activity resulted in higher visible light absorption which can be applied in light harvesting application [10–13]. However, none of previous studies were employed RSM in their works. Hence, in this work, the RSM was applied to determine the efficiency response since parameter optimization has been a major issue in solar cell fabrication.

In this study, the photoanode parameters namely TiO_2 thickness with amount of GQD were varied to determine the effect of photovoltaic performance of DSSC. RSM technique was employed to the factor level combinations that gave the best performance and reducing the number of sample, time and cost in preparing the samples [14-15]. Central composite design (CCD) under RSM was chosen based on polynomial model for best result. Then for analysis the right model will be suggested and analysis of variance (ANOVA) was done to analyze the different among variance and mean.

EXPERIMENTAL

Materials and Method

GQD was synthesis by exfoliation hydrothermal method using biochar and solvent in our lab. Titania powder of <29 nm in size was purchased from Sigma Aldrich. Fluorine doped Tin Oxide (FTO) coated glass with <15 Ω/sq of sheet resistance was purchased from Kaivo optoelectronic Technology. N-719 Dye, elctrolyte and polymer spacer of 25 μm was from Solaronix Switzerland. Finally platinum solution for counter electrode consist of isopropyl alcohol (IPA) and hexachloroplanitic acid hexahydrate was prepared in our lab.

Photoanode preparation and complete DSSC

For photoanode fabrication, a FTO glass with active area of 1 cm^2 was prepared by screen-printing technique using TiO_2 paste made by traditional method. The thickness of TiO_2 layer was varied from 5 μm to 20 μm. The thickness increment was added following by drying process in the oven at 80°C until desired thickness was achieved. The TiO_2 thickness was measured using Olympus 3D measuring laser microscope. Then the film was sintered at 450°C for 30 minutes. The film was cooled at 50°C before continuing by spin-coating method with different amount of graphene quantum dots (GQDs). Finally, the films were immersed in N-719 dye at room temperature for 24 hrs. Ethanol was used to clean the thin film to remove any loose dye particle. To make a complete cell of DSSC, an electrolyte was dropped between FTO glass of photoanode and counter electrode. Both electrodes were attached with 25 μm polymer spacer to form a sandwich structure of solar cell. Finally, a solar simulator was used to study the performance of current density and efficiency of DSSC

Design of experiment

Central composite design (CCD) of design expert software version 6.0.6 was employed to evaluate two independent variables namely TiO_2 thickness (X_1) and GQDs amount (X_2) are shown in Table 1. A selected variable and the ranges were based on reference as TiO_2 thickness [16–18] and amount GQD [19]. As a result, 13 samples were fabricated to fulfil this design with actual efficiency value as shown in Table 2. The efficiency values were obtained using solar simulator source meter (Keithly 2611, USA) at 100 mWcm^{-2} light intensity.

Table 1: Independent variable for photoanode modelling

Numeric Factor	**Name**	**Unit**	**low**	**High**
X_1	TiO_2 Thickness	(μm)	5	20
X_2	GQD amount	(μL)	0	50

Table 2: DSSC parameters using central composite model

Run	**X_1 TiO_2 Thickness**	**X_2 GQD amount**	**Response Efficiency (%)**
1	12.5	37.5	3.04
2	20.0	50.0	0.69
3	12.5	25.0	2.93
4	12.5	25.0	2.93
5	12.5	25.0	2.93
6	5.0	0	3.84
7	12.5	25.0	2.93
8	8.75	25.0	3.30
9	20.0	0	0.52
10	16.25	25.0	0.68
11	12.5	25.0	2.93
12	5.0	50.0	5.65
13	12.5	12.5	2.45

The relationship between the variable denoted as X_1 and X_2 and the response of efficiency Y, are expressed in Eq. 1 as below. Where f represents the response function

$$Y = f(X_1, X_2) \quad (1)$$

In this work, a polynomial model of two-level factorial design used for evaluating curvature together with quadratic term to present the model as in Eq. 2 below.

$$Y = \beta_0 + \Sigma\, \beta_i x_i + \Sigma\, \beta_{ii} x_i^2 + \Sigma\, \beta_{ij} x_i x_j + \mathcal{E} \quad (2)$$

Where β_0 is the constant term, β_i represent the coefficient of linear parameters, X_i represents the variables, β_{ii} represent the coefficients of the quadratic parameters and β_{ij} represent the coefficients of the interaction parameters and $\mathcal{E}$ is the residual associated with experiment. Hence the predicted efficiency solar cell, denoted as Y and the variables X_1 and X_2 namely thickness and GQD amount respectively, are explained as Eq. 3 below.

$$F(x) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 \quad (3)$$

RESULTS AND DISCUSSION

Development of Regression Model

After obtaining the efficiency value from solar simulator as shown in Table 2, a selected regression model based on the highest order polynomial was generated to represent the efficiency response of solar cell by empirical model and represent in Eq. 4.

$$\text{Efficiency, } Y = 4.958 - 0.231X_1 + 0.048\, X_2 - 0.182\, X_1 X_2 \quad (4)$$

Where X_1 = thickness of TiO_2 (5-20 μm), and X_2 = GQD (0-50 μL) as independent variables in this work. The linear terms of X_1 and X_2 represent the effect of the individual variable on the response efficiency. Predicted and actual values for DSSC efficiency are represented in Figure 2 below with determination coefficient of determination (R^2) at 0.9651. The R^2 value is approximately near unity between actual and predicted efficiency value. This proved the aggrement of the model applied in this work.

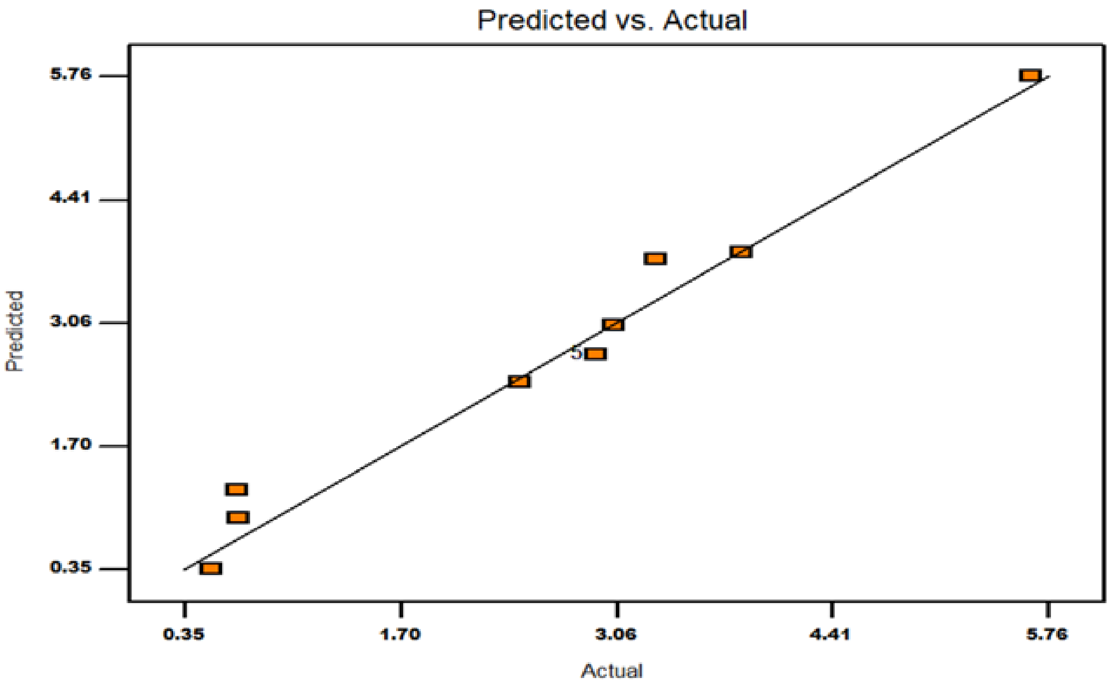

Figure 1: Plot of predicted and actual efficiency of DSSC

Current density - Voltage measurement

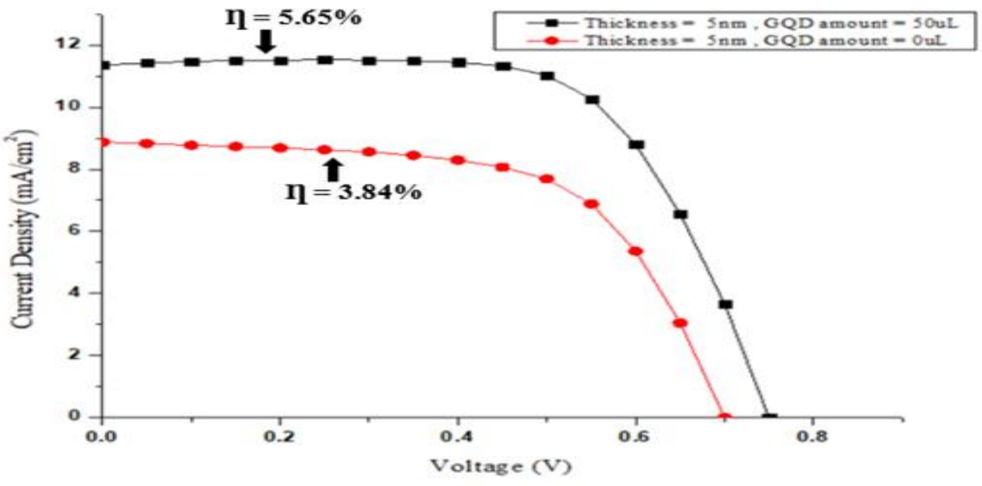

Figure 2: J-V curve of DSSC after GQD spin coated at 0 μL and 50 μL on 5 nm TiO_2 layer thickness, resulted efficiency at 3.84% and 5.65% respectively

The J-V curve shown the best solar cell prepared at 5 μm TiO_2 thickness and 50 μL GQD generated current density of 11.36 $mA.cm^{-2}$ and open-circuit voltage of 0.75 V (5.65% efficiency). However, at the same thickness and 0 mL GQD, the cell produced

8.88 mA.cm^{-2} and open-circuit voltage of 0.70 V (3.84% efficiency). The J-V performance was improved may be due to GQD absorb efficiently on TiO_2 surface at 5 μm thickness and GQD photoluminescence (PL) property. PL property belong to GQD may absorb the ultraviolet light from sun and emit it to the visible region. Hence GQD improve visible light harvesting when photon penetrate on dye sensitizer surface [19]. Hence, GQDs allow more electron-hole pair [10] and generated higher current density Jsc and ŋ of DSSC. The optimum TiO_2 thickness is important because an exciton electron can move to conductive base easily. When the thickness was too high, it allowed the recombination occurred in the cell which reduced the efficiency value. Figure 3, shows the relationship between efficiency and TiO_2 thickness and GQD amount for this work.

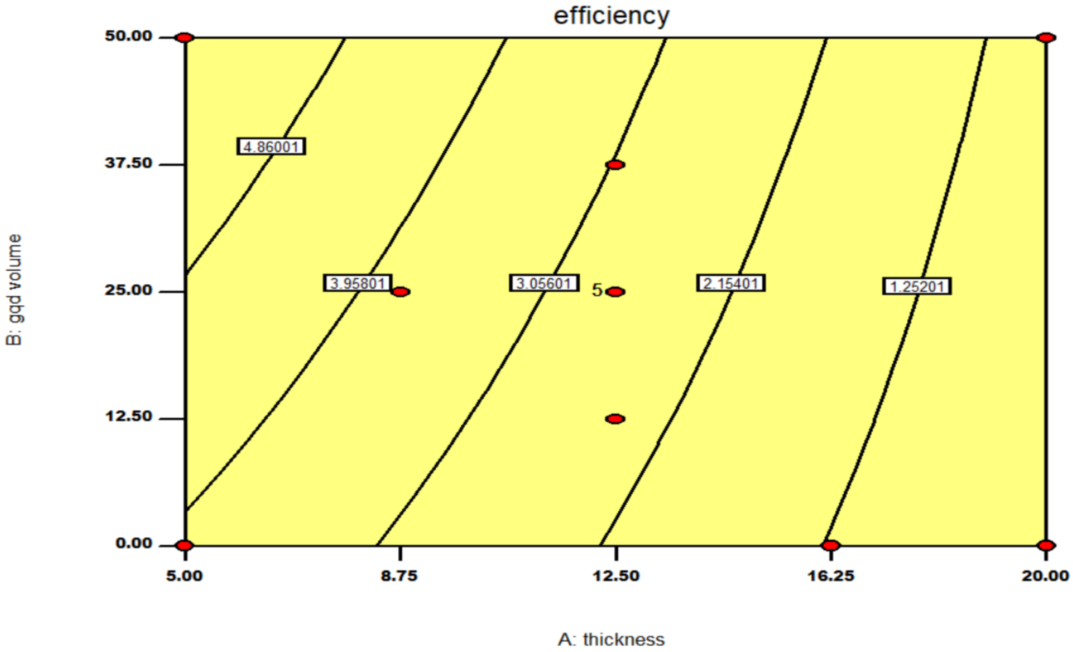

Figure 3: Plot of response efficiency with variable TiO_2 thickness and GQD amount.

CONCLUSION

RSM is a good tool to study the efficiency response of DSSC by varying the range of DSSC variables such as TiO_2 thickness and GQD amount. The best photon-to-current efficiency obtained when the thickness was 5 μm and 50 μL GQD amount was spin coated at 5.65% compare to 3.84% at 0 μL GQD amount. The RSM model will benefit the solar cell research and industry where the optimization of variable parameter is a major interest in the future.

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