

## Research Article

# Adsorption Equilibrium and Kinetics of *Gardenia Blue* on $\text{TiO}_2$ Photoelectrode for Dye-Sensitized Solar Cells

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Nanostructured porous  $\text{TiO}_2$  paste was deposited on the FTO conductive glass using squeeze printing technique in order to obtain a  $\text{TiO}_2$  thin film with a thickness of  $10\ \mu\text{m}$  and an area of  $4\ \text{cm}^2$ . *Gardenia blue* (GB) extracted from *Gardenia jasminode Ellis* was employed as the natural dye for a dye-sensitized solar cell (DSSC). Adsorption studies indicated that the maximum adsorption capacity of GB on the surface of  $\text{TiO}_2$  thin film was approximately  $417\ \text{mg GB/g TiO}_2$  photoelectrode. The commercial and natural dyes, N-719 and GB, respectively, were employed to measure the adsorption kinetic data, which were analyzed by pseudo-first-order and pseudo-second-order models. The energy conversion efficiency of the  $\text{TiO}_2$  electrode with successive adsorptions of GB dye was about 0.2%.

## 1. Introduction

Dye-sensitized solar cells (DSSCs) are devices for the conversion of visible light into electricity based on sensitization of wide-bandgap semiconductors. The sensitization approach enables the generation of electricity with irradiation of energy lower than the bandgap of the semiconductor [1]. DSSC is assembled with an anode of conductive glass coated with platinum, a cathode of  $\text{TiO}_2$  porous film on a conductive glass substrate anchored a monolayer of dyes, and an electrolyte of certain organic solvent containing a redox couple, such as iodide/triiodide [2]. It is well known that photoelectrochemical cells can be used for solar energy conversion into electricity, as well as for production of chemical fuels [3, 4]. A key issue in the development of such devices is the optimization of interactions between the sensitizer dye and the nanocrystalline metal oxide and in particular optimization of the injection process [5, 6]. The absorption spectrum of the dye and the anchorage of the dye to the surface of  $\text{TiO}_2$  are important parameters determining the efficiency of the cell [2]. Since dye plays an important role in absorbing visible light and transferring photon energy into electricity, much

attention has been paid to survey the effective sensitizer dyes. Natural dyes provide a viable alternative to expensive organic dyes for DSSCs.

Many natural dyes including chlorophyll, anthocyanin [7–9], carotenoids [10], cyanidin, crocetin [11], and tannin [12] have been tested over the last two decades as suitable sensitizers for DSSCs. It has been generally known that the photovoltaic performance of DSSC is highly influenced by adsorption properties of dyes on  $\text{TiO}_2$  film. Unfortunately, the studies on the adsorption properties (i.e., equilibrium and kinetics) of dye molecules have so far been very limited. In this work, the influence of the adsorption properties between the GB dye and the  $\text{TiO}_2$  thin film on the energy conversion efficiency of the DSSCs was systematically investigated on the basis of the photovoltaic performance calculated from the *I-V* curves. For this, experimental and theoretical studies on the adsorption equilibrium and kinetics were carried out for the control of the adsorption amount and to understand the mechanism of adsorption of GB as a natural photosensitizer on  $\text{TiO}_2$  thin films. The equilibrium data were fitted by the Langmuir isotherm model and adsorption kinetic data

obtained under different temperatures (288, 298, and 308 K) were analyzed by employing the pseudo-first-order and pseudo-second-order models.

## 2. Experimental

The DSSCs were composed with dye-adsorbed TiO<sub>2</sub> photoelectrode, Pt counter electrode, and the liquid electrolyte. The liquid electrolyte is between the TiO<sub>2</sub> photoelectrode and Pt counter electrode. The TiO<sub>2</sub> photoelectrode was prepared by TiO<sub>2</sub> paste (DSL 18NR-T Dyesol Co.). The TiO<sub>2</sub> paste was coated on the FTO glass by squeeze printing, and the resulting coated electrode was heat-treated at 450°C for 30 min; the heating rate was 5°C/min. The active area of the photoelectrode was 2.0 × 2.0 cm<sup>2</sup>, and the thickness of TiO<sub>2</sub> photoelectrode was about 10 μm. The photoelectrode with the deposited TiO<sub>2</sub> was weighed by a digital balance to obtain the total weight of the TiO<sub>2</sub> thin film and FTO conductive glass. The purpose of measuring the samples before and after the deposition of the TiO<sub>2</sub> thin film is to evaluate the weight of the TiO<sub>2</sub> thin film deposited on each photoelectrode before starting the dye adsorption experiment. To prepare the counter electrode, Pt-Sol (Solaronix, Pt catalyst/SP) was coated onto FTO glass using a squeeze printing method. The coated paste was heat-treated at 450°C for 30 min with a heating rate of 5°C/min. The redox electrolyte consisted of 0.3 M 1,2-dimethyl-3-propylimidazolium iodide (Solaronix), 0.5 M LiI (Aldrich), 0.05 M I<sub>2</sub> (Aldrich), and 0.5 M 4-tert-butylpyridine (4-TBP, Aldrich) and 3-methoxy-propionitrile (3-MPN, Fluka) as a solvent.

GB was purchased from Naju Nature Dyeing Culture Center (Korea) and N-719 synthetic dye was obtained from Solaronix (Switzerland). All other chemical reagents were guaranteed reagent grade. Molecular structures of GB and N-719 are shown in Figure 1. The typical process for measuring the amount dye adsorbed on TiO<sub>2</sub> thin film was measured by completely desorbing the adsorbed dye molecules from the TiO<sub>2</sub> thin film using NaOH solution. However, this method is complex and gives an inaccurate measure of the amount of dye adsorbed on the TiO<sub>2</sub> thin film. To precisely measure the amount adsorbed without a desorption step from the TiO<sub>2</sub> thin film, a novel adsorption apparatus was made in our laboratory. The adsorption apparatus consists of a water circulation jacket, vessel, photoelectrode holder, magnetic stirrer bar, and TiO<sub>2</sub> coated thin film. The water circulation jacket was connected to a constant temperature water bath. The volume of the vessel was approximately 25 mL and that of the dye solution was 20 mL. To prevent the stirrer bar from destroying the TiO<sub>2</sub> thin film, the distance between the bottom of the vessel and TiO<sub>2</sub> thin film is 3 mm. In order to improve the adsorption efficiency of the dyes on the TiO<sub>2</sub> thin film in the adsorption apparatus, the coated TiO<sub>2</sub> surface of the photoelectrode was placed downwards in the photoelectrode holder. To measure the amount of dye adsorbed on the TiO<sub>2</sub> thin film without a desorption step, samples were taken periodically using a micropipette. The concentrations of N-719 and GB solutions adsorbed on the TiO<sub>2</sub> thin film were analyzed by a UV spectrophotometer

(UV-1601A, Shimadzu) at 522 and 593 nm, respectively. The amounts of N-719 and GB at equilibrium on the TiO<sub>2</sub> thin film were calculated from

$$q = \frac{(C_0 - C)V}{W}, \quad (1)$$

where  $q$  (mg/g) is equilibrium amount adsorbed of the dyes on the TiO<sub>2</sub> thin film.  $C_0$  and  $C$  (mg/L) are the initial and equilibrium liquid phase concentrations of the dyes.  $V$  (L) is the volume of the solution and  $W$  (g) is the mass of the TiO<sub>2</sub> thin film. The photovoltaic properties were investigated by measuring the  $I$ - $V$  characteristics under irradiation of white light from a 200 W Xenon lamp (Mc Science, Korea). The incident light intensity and the active cell area were 100 mW/cm<sup>2</sup>.

## 3. Results and Discussion

DSSCs are known to be closely related to the equilibrium amount of adsorbed dye on TiO<sub>2</sub> thin film [13, 14]. The adsorption characteristics of the GB on TiO<sub>2</sub> thin film and also N-719 for the comparison purpose were evaluated on the basis of adsorption equilibrium and kinetic studies. The adsorption capacity of GB and N-719 on TiO<sub>2</sub> thin film was evaluated by measuring the adsorption equilibrium data. As expected, the adsorption amount of GB on TiO<sub>2</sub> thin film was greater than that of N-719 as shown in Figure 2. The isotherm parameters of  $q_m$  and  $b$  were 417.37 mg/g and 0.029 L/mg for GB and 417.37 mg/g and 0.029 L/mg for N-719, respectively. The Langmuir model was used to correlate our experimental equilibrium data:

$$q = \frac{q_m b C_e}{1 + b C_e}, \quad (2)$$

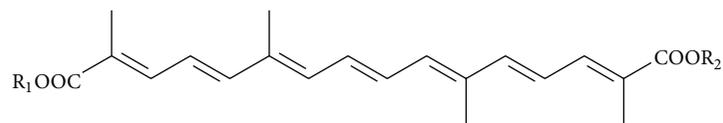
where  $C_e$  is the supernatant concentration in the equilibrium state of the system (mg/L),  $b$  is the Langmuir affinity constant, and  $q_m$  is the maximum adsorption capacity of the material (mg/g), assuming the uptake of a monolayer of adsorbate by the adsorbent.

To find the parameters for each adsorption isotherm, the linear least square method and pattern search algorithm were used. The value of the mean percentage error has been used as a test criterion for the fit of the correlations. The mean percent deviation between experimental and predicted values was obtained using

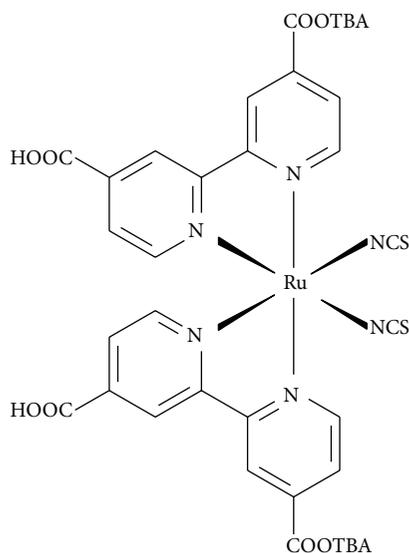
$$\text{error(\%)} = \frac{100}{N} \sum_{k=1}^N \left[ \frac{|q_{\text{exp},k} - q_{\text{mol},k}|}{q_{\text{exp},k}} \right], \quad (3)$$

where  $q_{\text{mol},k}$  is each value of  $q$  predicted by the fitted model,  $q_{\text{exp},k}$  is each value of  $q$  measured experimentally, and  $N$  is the number of experimental data. The parameters and the average percent differences between measured and calculated values for GB and N-719 on TiO<sub>2</sub> thin film are given in Table 1. The Langmuir model fitted well the experimental data of GB and N-719 on TiO<sub>2</sub> thin film.

The absorption spectra of GB and N-719 on TiO<sub>2</sub> thin film in terms of adsorption time (1, 2, 3, and 5 h) were



Gardenia blue dye



N-719 dye

FIGURE 1: Chemical structure of *Gardenia blue* and N-719 (N-719 chemical name is cis-diisothiocyanato-bis(2,20-bipyridyl-4,40-dicarboxylato) ruthenium(II) bis (tetrabutylammonium); COOTBA is carboxylatotetrabutylammonium).

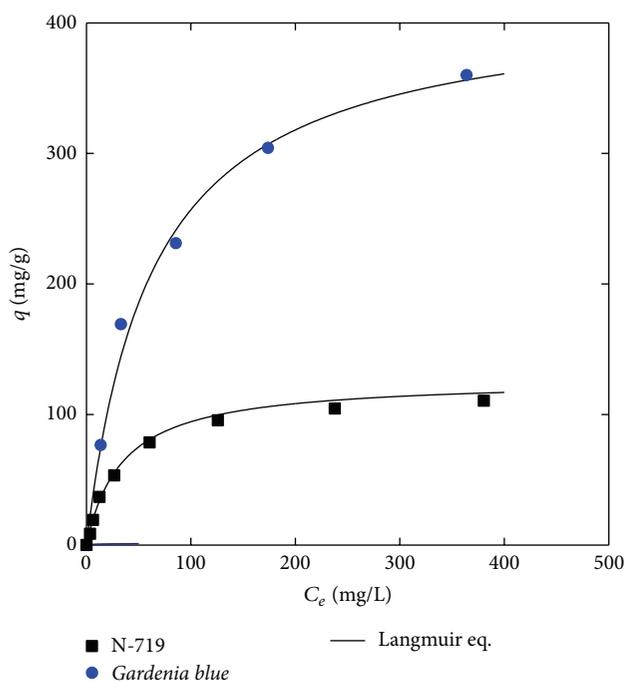


FIGURE 2: Adsorption equilibrium isotherms of *Gardenia blue* and N-719 on  $\text{TiO}_2$  thin film at 298 K.

TABLE 1: Langmuir isotherm constants of *Gardenia blue* and N-719 on  $\text{TiO}_2$  thin film.

Isotherm type	Parameters	<i>Gardenia blue</i>	N-719
Langmuir	$q_m$	417.37	126.98
	$b$	0.016	0.029
	Error (%)	4.71	4.14

shown in Figures 3 and 4. Obviously, *GB* dye mainly absorbs lights in the wavelength ranges of about 500–700 nm with its maximum absorption much higher than that of N-719. On the other hand, an absorption of light is observed for N-719 dye in the wavelength range of about 400–600 nm. Also those figures show the absorption spectra of the  $\text{TiO}_2$  thin films soaked in *GB* and N-719 dyes for 1, 2, 3, and 5 h. It is apparently found that the absorption curve remains nearly the same absorption extent; that is, the adsorption of dye on  $\text{TiO}_2$  thin films attained the saturated state, after the soaking duration reached 3 h for the N-719 dye soaked  $\text{TiO}_2$  thin film and 5 h for the *GB*. The results indicate a higher adsorption rate of N-719 on the  $\text{TiO}_2$  thin film, leading to the more adsorption of N-719 dye.

The mechanism of adsorption often involves chemical reaction between functional groups present on the  $\text{TiO}_2$  thin

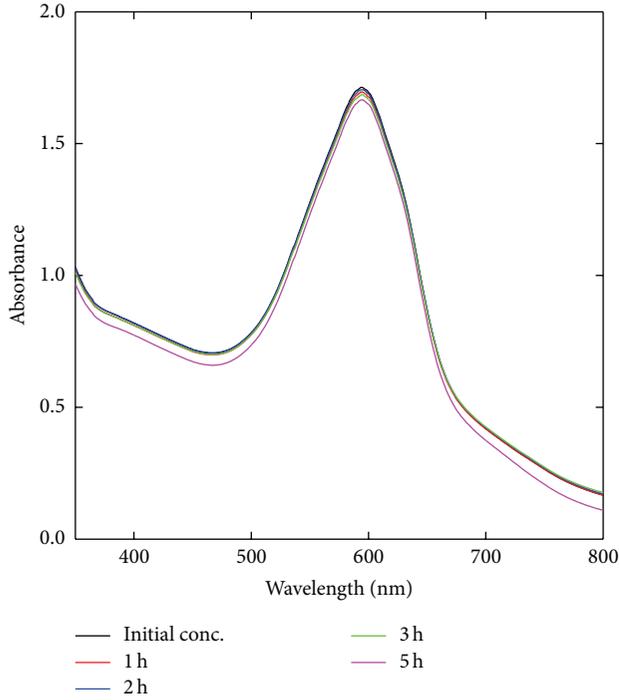


FIGURE 3: Variation of absorbance of *Gardenia blue* in terms of adsorption time on  $\text{TiO}_2$  thin film.

film and the *GB*. Therefore, it is meaningful to investigate the kinetic behaviors in terms of temperatures. Figures 5–8 show the kinetic data obtained in terms of different temperatures (288, 298, and 308 K). The order of  $\text{TiO}_2$  thin film and *GB* interactions has been described by using various kinetic models. In this work, we have used the pseudo-first-order model derived by Lagergren [15] and Ho [16]:

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1}{2.303}t, \quad (4)$$

where  $q_{eq}$  and  $q_t$  are the amounts (mg/g) of adsorbed dyes on  $\text{TiO}_2$  thin film at equilibrium and at time  $t$ , respectively, and  $k_1$  is the rate constant of the pseudo-first-order adsorption process (1/min). The plot of  $\log(q_{eq} - q_t)$  versus  $t$  gives a straight line for first-order kinetics, as shown in Figure 5. The calculated parameters of the pseudo-first-order kinetic model are listed in Table 2. The determined rate constants of  $k_1$  and  $q_{cal}$  were in the range of  $2.128 \times 10^{-2}$ – $2.251 \times 10^{-2} \text{ min}^{-1}$  and 283.8–399.9 mg/g, respectively. The correlation coefficients ( $R^2$ ) of the pseudo-first-order model for the linear plots of  $\text{TiO}_2$  thin film are nearly close to 1. However, the values obtained from this kinetic model gave reasonable values, which were too low compared with those obtained experimentally. This suggested that the adsorption process of *GB* on  $\text{TiO}_2$  thin film does not follow the Lagergren expression for pseudo-first-order adsorption.

Several authors report that the second-order kinetics can also be applied to these interactions in certain specific cases.

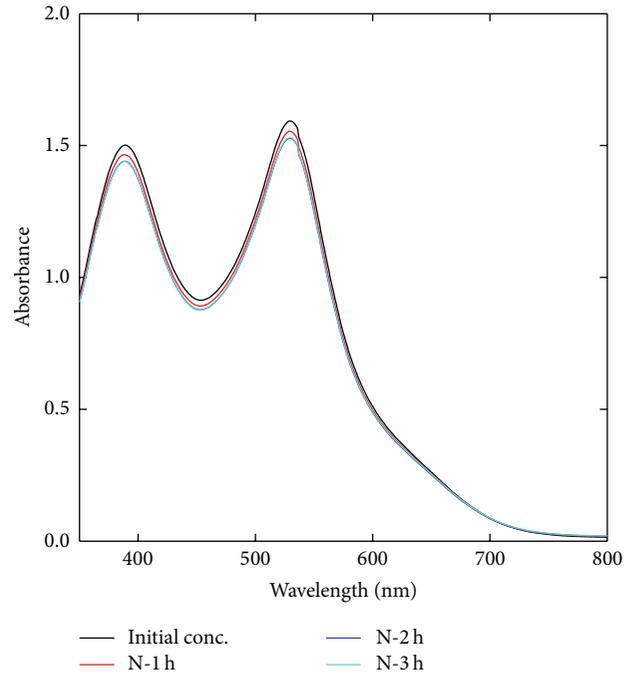


FIGURE 4: Variation of absorbance of N-719 in terms of adsorption time on  $\text{TiO}_2$  thin film.

The pseudo-second-order kinetic equation [17] is expressed as

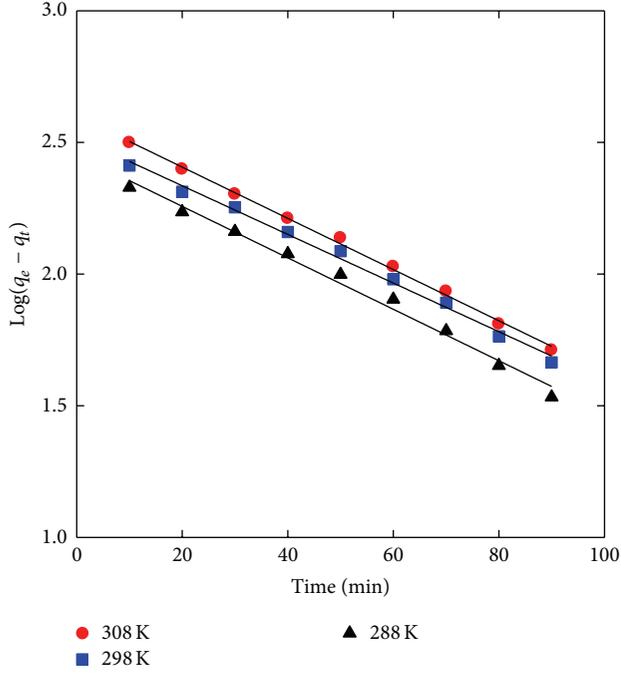
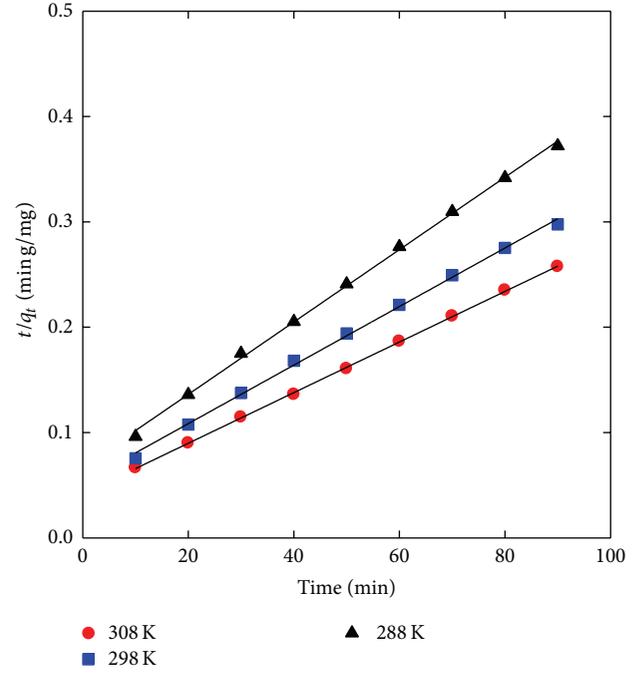
$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}}t, \quad (5)$$

where  $k_2$  is the rate constant of pseudo-second-order kinetic model (g/mg min). The rate parameters  $k_2$  and  $q_{cal}$  can be directly obtained from the intercept and slope of a plot of  $t/q_t$  versus  $t$ , as shown in Figure 6. The values of  $k_2$  and  $q_{cal}$  are shown in Table 2. The determined rate constants of  $k_2$  and  $q_{cal}$  were in the range of  $1.381 \times 10^{-4}$ – $1.748 \times 10^{-4}$  (g/mg min) and 291.1–416.3 mg/g, respectively. The values of  $k_2$  decreased with increasing temperature of *GB* solution, presumably due to the enhanced mass transfer of *GB* molecules to the surface of the  $\text{TiO}_2$  thin film. As shown in Figure 7, a higher adsorption capacity can be observed at 308 K. And concentration decay curves of *GB* on  $\text{TiO}_2$  thin film could be represented by pseudo-second-order kinetic model. As shown from Table 2, the correlation coefficient ( $R^2$ ) has an extremely high value (0.999) and closer to unity for the pseudo-second-order kinetic model compared to the value of pseudo-first-order kinetic model. The calculated equilibrium sorption capacity ( $q_{cal}$ ) is consistent with the experimental data. These results explain that the pseudo-second-order sorption mechanism is predominant and that the overall rate constant of sorption process appears to be controlled by a chemisorption process.

It is important to estimate the mass transfer coefficient for *GB* on  $\text{TiO}_2$  thin film. There are several correlations for estimating the film mass transfer coefficient,  $k_f$ , in a batch system. In this work, the  $k_f$  was estimated from the initial

TABLE 2: Kinetic parameters of *Gardenia blue* on TiO<sub>2</sub> thin film.

Temperature (K)	$q_{cal}$ (mg/g)	Pseudo-first-order		$q_{cal}$ (mg/g)	Pseudo-second-order		$q_{eq}$ (mg/g)
		$k_1 \times 10^{-2}$ (min <sup>-1</sup> )	$R^2$		$k_2 \times 10^{-4}$ (g/mg min)	$R^2$	
288	283.8	2.251	0.989	291.1	1.748	0.999	293.3
298	331.1	2.128	0.994	359.8	1.461	0.998	353.1
308	399.9	2.241	0.997	416.3	1.381	0.999	411.5

FIGURE 5: Linearized pseudo-first-order kinetic model of *Gardenia blue* on TiO<sub>2</sub> thin film at different temperature.FIGURE 6: Linearized pseudo-second-order kinetic model of *Gardenia blue* on TiO<sub>2</sub> thin film at different temperature.

concentration decay curve when the diffusion resistance did not prevail. The transfer rate of any species to the external surface of the thin film,  $N_A$ , can be expressed by

$$N_A = k_f A_s (C - C_s), \quad (6)$$

where  $N_A$  is the rate of mass transfer of the solutions to the external surface of TiO<sub>2</sub> thin film,  $k_f$  is the film mass transfer coefficient (m/sec), and  $A_s$  is the surface area of TiO<sub>2</sub> thin film (cm<sup>2</sup>). Rearranging of (6) and approximating for a batch system with an adsorption time of less than 300 seconds, the following can be obtained [18]:

$$\ln\left(\frac{C}{C_0}\right) = -k_f A_s \frac{t}{V_s}, \quad (7)$$

where  $V_s$  is the volume of solution (cm<sup>3</sup>) and  $A_s$  is the effective external surface area of TiO<sub>2</sub> thin film. When  $\ln(C/C_0)$  is plotted versus time, a straight line, with slope  $-k_f A_s/V_s$ , is obtained (Figure 8). The values of the film mass transfer coefficients,  $k_f$ , for *GB* in terms of temperature on TiO<sub>2</sub> thin film were  $2.193 \times 10^{-8}$  (for 288 K),  $2.032 \times 10^{-8}$  (for 298 K), and  $1.874 \times 10^{-8}$  m/s (for 308 K), respectively.

The coefficients of determination between measurement and calculation from the slope are 0.994, 0.997, and 0.994.

Figure 9 shows the incident photon-to-current conversion efficiency (IPCE) of DSSCs with *GB* and N-719 on a transparent nanocrystalline TiO<sub>2</sub> thin film. The IPCE is defined as the ratio of the number of electrons generated by light in the external circuit to the number of incident photons as follows:

$$\text{IPCE}(\lambda) = \frac{1240 \times J_{sc} [\mu\text{A}/\text{cm}^2]}{\lambda (\text{nm}) \times P [\text{W}/\text{m}^2]}. \quad (8)$$

The light harvesting efficiency is related to the concentration of dye adsorbed by the TiO<sub>2</sub> thin film. At 320 nm, the maximum IPCE was at the absorption maximum of *Gardenia blue*. The IPCE value was 14.5%, whereas that of N-719 was 37.4%. The IPCE value of N-719 with a maximum value of 68.5% at 530 nm was significantly higher than that of *Gardenia blue*, indicating that the amount adsorbed on the TiO<sub>2</sub> thin film was large and that strong chemical bonding existed between the TiO<sub>2</sub> and the dye.

The photovoltaic parameters were obtained through measuring photocurrent-voltage (*I-V*) curves as shown in

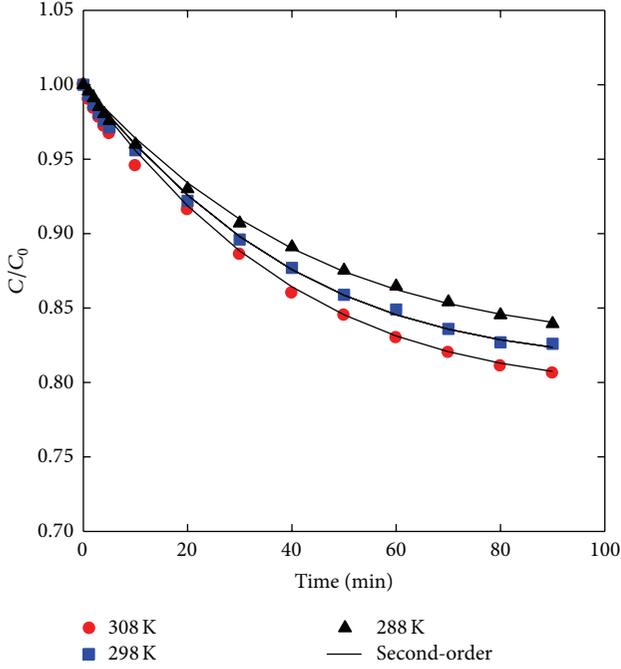


FIGURE 7: Concentration decay curves of *Gardenia blue* on  $\text{TiO}_2$  thin film.

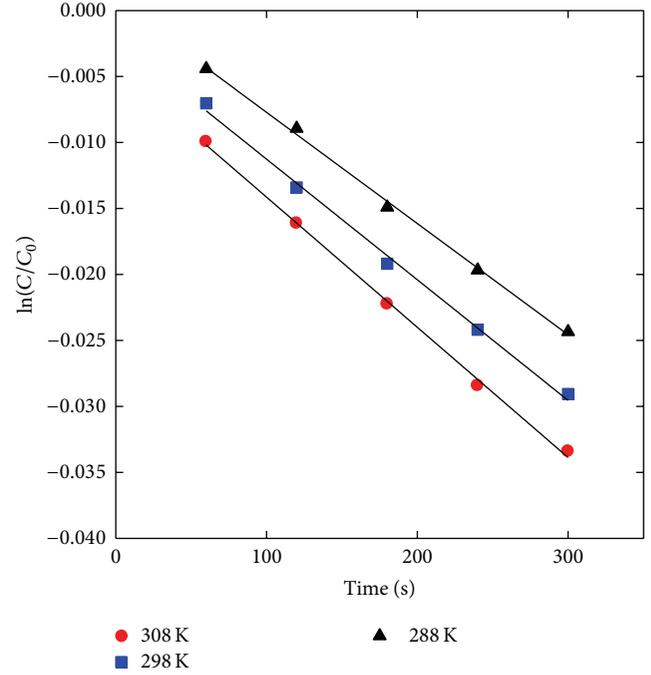


FIGURE 8: Determination of  $k_f$  from plots of  $\ln(C/C_0)$  versus time for *Gardenia blue* on  $\text{TiO}_2$  thin film.

Figure 10. The  $I$ - $V$  curves were used to calculate the short-circuit current ( $I_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor (FF), and overall conversion efficiency ( $\eta_{eff}$ ) of the DSSCs. Figure 10 shows the photocurrent-voltage ( $I$ - $V$ ) curves of GB and commercial dye solar cell. The fill factor (FF) and overall energy efficiency ( $\eta$ ) are determined by the following equation:

$$FF = \frac{I_{max} \times V_{max}}{I_{sc} \times V_{oc}},$$

$$\eta (\%) = \frac{P_{out}}{P_{in}} \times 100 = \frac{I_{max} \times V_{max}}{P_{in}} \times 100 \quad (9)$$

$$= \frac{I_{sc} \times V_{oc} \times FF}{P_{in}} \times 100,$$

where  $I_{sc}$  is the short-circuit current density ( $\text{mA}/\text{cm}^2$ ),  $V_{oc}$  is the open-circuit voltage (V),  $P_{in}$  is the incident light power, and  $I_{max}$  ( $\text{mA}/\text{cm}^2$ ) and  $V_{max}$  (V) are the current density and voltage in the  $I$ - $V$  curve at the point of maximum power output, respectively. The dye-sensitized solar cell assembled with GB had an open-circuit voltage of 0.56 V and a short-circuit current density of  $0.55 \text{ mA}/\text{cm}^2$  at an incident light intensity of  $100 \text{ mW}/\text{cm}^2$ . The power conversion efficiency of GB was 0.199%. However, it was 7.2% in the case of the DSSC made from the commercial dye (N-719), with an open-circuit voltage of 0.70 V and a short-circuit current density of  $17.1 \text{ mA}/\text{cm}^2$ . The  $V_{oc}$  of GB dye is lower than that of N-719 dye, because of the molecular structure of the natural dye which mostly has hydroxyl (OH) ligands and O ligands and lacks the carboxyl ( $-\text{COOH}$ ) ligands of N-719 dye. The  $-\text{COOH}$  ligands will combine with the hydroxyl groups of

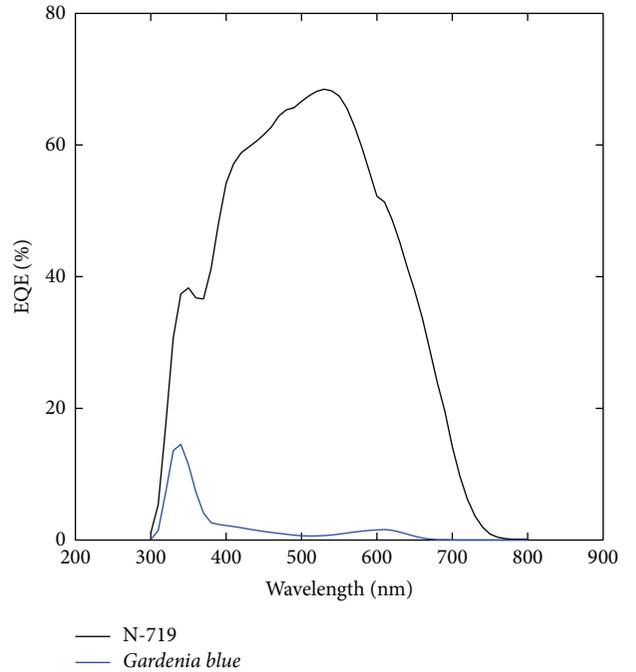


FIGURE 9: IPCE values of *Gardenia blue* and N-719.

the  $\text{TiO}_2$  particles to produce the ester moiety and boost the coupling effect of the electrons in the  $\text{TiO}_2$  conduction band so as to provide a rapid electron-transport rate.

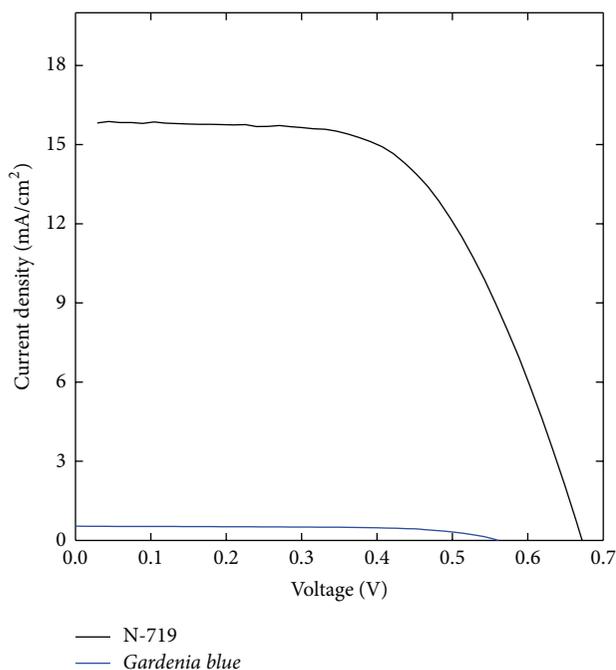


FIGURE 10: *I-V* curves of *Gardenia blue* and N-719.

#### 4. Conclusions

The commercial N-719 and natural *GB* dyes were employed to measure in situ the adsorption equilibrium and kinetic data in an adsorption small chamber. The amount of adsorbed natural dye increased with increasing temperature and adsorption isotherm of the dyes was fitted with the Langmuir isotherm. The kinetics data were better fitted with the pseudo-second-order model than with the pseudo-first-order model. The DSSC fabricated in this work gave a  $V_{oc}$  of 0.56 V and an  $I_{sc}$  of 0.55 mA/cm<sup>2</sup> for an incident light intensity of 100 mW/cm<sup>2</sup>. The power conversion efficiency of *Gardenia blue* was about 0.2%.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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