

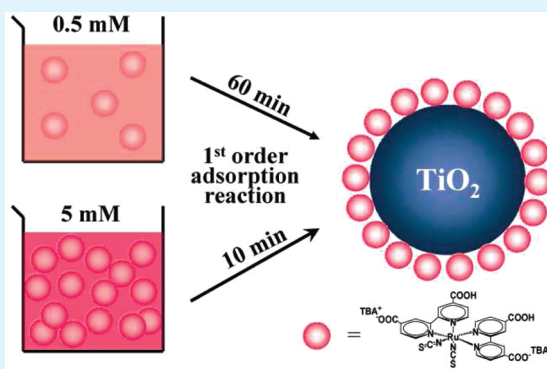
Pseudo First-Order Adsorption Kinetics of N719 Dye on TiO₂ Surface

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ABSTRACT: We have investigated the adsorption kinetics of Ru-based N719 dye on TiO₂ surface in dye-sensitized solar cell using 0.5 mM and 5 mM dye solutions. The amount of adsorbed dye on TiO₂ surface of ca. 5 μm-thick film was measured as a function of immersion (adsorption) time. The amount of adsorbed dye increases with increasing the adsorption time and keeps constant after saturation. Completion of dye adsorption is found to be more than 5 times faster in 5 mM than in 0.5 mM. Since the change of dye concentration is negligible compared to that of number of TiO₂ adsorption site, reaction order and rate constant can be estimated from a pseudo reaction. Among the zeroth-, first-, and second-order simulation, the observed data follow first order reaction for both 0.5 mM and 5 mM cases. The rate constant is estimated to be 0.504 min⁻¹ for 5 mM and 0.094 min⁻¹ for 0.5 mM, which indicates that completion of dye adsorption is about 5 times shorter in 5 mM than in 0.5 mM. This is consistent with the observed adsorption time difference. Except for the difference in adsorption kinetics, best cell efficiency is similar regardless of dye solution concentration.

KEYWORDS: dye-sensitized solar cell, reaction kinetics, pseudo first order, adsorption time, adsorption concentration



INTRODUCTION

Since discovery of dye-sensitized solar cell (DSSC) by O'Regan and Grätzel in 1991,¹ DSSC has attracted much attention because of its low-cost, colorful, and semitransparent characteristics. Solar-to-electrical conversion efficiency has reached 11% based on ruthenium bipyridyl complex sensitizer (coded as N719), nanocrystalline TiO₂, and iodine/iodide redox electrolyte.^{2–6} DSSC device can be fabricated by assembling a photoanode, comprising a dye-adsorbed TiO₂ film on a transparent conductive oxide (TCO) substrate, and a cathode, comprising a Pt-coated TCO substrate, where redox electrolyte is filled in between two electrodes. For dye adsorption, the TiO₂ film annealed at around 500 °C is immersed in the 0.3–0.5 mM dye solution for 24 h at ambient temperature,^{7–9} or a few hours at around 40–50 °C.^{10,11} When considering overall fabrication process, dye adsorption process is a kind of rate-determining step because of long adsorption time. Therefore, time for overall fabrication process will be reduced if dye adsorption is quickly completed. A method to reduce the dye adsorption time was reported¹² where dye adsorption was completed within 10 min in the case where the dye concentration increased from 0.5 to 20 mM. However, the basis for the faster adsorption at higher concentration has not been investigated. A similar phenomenon was observed, where dye adsorption was performed by pumping the dye solution through the sealed cavity and dyeing time took 5–10 min when the dye solution concentration was 8.6 mM.¹³ This report did not explain the reason for the rapid adsorption when increasing dye concentration. Rapid dye adsorption process is important from an industrial point of view. Although high concentration of dye solution has been found to accelerate dye adsorption, effect of dye concentration on adsorption kinetics has not been studied.

We have investigated dye adsorption kinetics from 0.5 and 5 mM N719 dye solutions. The amount of N719 dye adsorbed on TiO₂ film was measured with time, from which the adsorption reaction order and reaction constant is evaluated. In addition, the effect of the degree of adsorption on photovoltaic property is also investigated for the case of 0.5 and 5 mM N719 dye solution.

EXPERIMENTAL SECTION

Fluorine-doped tin oxide (FTO) glasses (Pilkington, TEC-8, 8 Ω/sq, 2.3 mm thick) were cleaned with ethanol. A thin TiO₂ underlayer formed on a FTO surface by spin coating of Ti (IV) bis-(ethylacetoacetato) diisopropoxide (Aldrich, 75%) solution (0.1 M in 1-Butanol), followed by heating at 500 °C for 15 min. TiO₂ nanoparticles were hydro-thermally synthesized using titanium isopropoxide (Aldrich, 97%) at 230 °C for 12 h, as described elsewhere.¹⁴ TiO₂ paste, composed of the synthesized TiO₂ particles, terpeneol (Aldrich, 99.5%), ethyl cellulose (Aldrich, 46 cP in 5% in 80/20 toluene/EtOH) and lauric acid (Fluka, 96%) with nominal ratio of 1.25: 4: 0.3: 0.1, was coated on a thin TiO₂ underlayer coated FTO glass by doctor-blade method, which was annealed at 550 °C for 60 min. The annealed TiO₂ films were sensitized with 0.5 mM or 5 mM N719 dye at 40 °C, where N719 stands for Ru[LL'(NCS)₂], L = 2,2'-bipyridyl-4,4'-dicarboxylic acid, L' = 2,2'-bipyridyl-4,4'-ditetrabutylammonium carboxylate (Esolar, Taiwan). The amount of the adsorbed dye was monitored with time. The adsorbed dye was quantitatively determined from the absorbance at 510 nm measured by Agilent 8453 UV–vis spectrophotometer, where dye was desorbed by immersing the dye-covered TiO₂ films in 10 mL of 0.1 M NaOH aqueous solution for 10 min.

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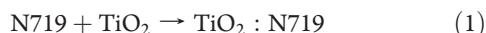
To investigate effect of adsorption time on photovoltaic performance, we assembled dye-sensitized TiO₂ electrode with Pt counter electrode. Pt counter electrode was prepared by spreading 200 μL of 7 mM of H₂PtCl₆·6H₂O in 2-propanol on a 1.5 \times 2 cm sized FTO glass, which was heated at 400 $^{\circ}\text{C}$ for 15 min in air. The dye-adsorbed TiO₂ electrode and the Pt counter electrode were sealed with 25 μm -thick Surlyn (SX1170–25, Solaronix) at a pressure of 230 Kpa/cm² and a temperature of about 100 $^{\circ}\text{C}$. The electrolyte was composed of 0.7 M 1-methyl-3-propyl-imidazolium iodide (MPII), 0.03 M I₂ (Aldrich, 99.8%), 0.05 M guanidinium thiocyanate (GuSCN) (Aldrich, 97%) and 0.5 M 4-*tert*-butylpyridine (Aldrich, 96%) in acetonitrile (Fluka, 99.9%) and valeronitrile (Aldrich, 99.5%) (85:15 v/v). The active area was measured by a digital microscope camera (DCMe 500) equipped with an image-analysis program (Leopard 2009). TiO₂ film thickness was measured by alpha-step IQ surface profile (KLA Tencor).

Photocurrent and voltage were measured from a solar simulator (Oriol Sol 3A class AAA) equipped with 450 W xenon lamp (Newport 6279NS) and a Keithley 2400 source meter. Light intensity was adjusted with the NREL-calibrated Si solar cell having KG-2 filter for approximating one sun illumination (100 mW/cm²). The cell was covered with an aperture mask to measure photocurrent and voltage accurately. Surface area of TiO₂ particle was measured by Brunauer–Emmett–Teller (BET) setup (Micromeritics Instrument Corp. ASAP 2020).

RESULTS AND DISCUSSION

Figure 1 shows the amount of the adsorbed N719 dye on the TiO₂ film as a function of dipping time (referred to as hereafter adsorption time), where TiO₂ film thickness is about 5.3 μm and average particle diameter is about 20 nm. For the case of 0.5 mM concentration, the adsorbed amount remains unchanged after 60 min, which indicates that dye adsorption is nearly completed in 60 min. On the other hand, higher concentration of 5 mM terminates completion of dye adsorption within 10 min. A slightly decreased adsorption amount for more than 10 min dipping in 5 mM solution may be due to competition reaction between dye-to-TiO₂ adsorption and dye-to-dye interaction because of the increased dye solution concentration. It was reported that the increase in N719 dye solution concentration was found to result in multilayer adsorption.¹⁵ Therefore, 10 min-adsorption is likely to lead to multilayer, forming dye agglomerates, which increases the amount of the adsorbed dye. In addition, the dye agglomerates are likely to tend to be desorbed because of weak binding characteristics. Longer adsorption time is thus expected to decrease the amount of the adsorbed dye.

On the basis of the results in Figure 1, we have tried to estimate adsorption reaction order and reaction constant. We denote the adsorbed N719 dye on TiO₂ as TiO₂:N719. The adsorption kinetics is then expressed by concentration change with time (t), that is, $d[\text{TiO}_2:\text{N719}]/dt$. When $d[\text{TiO}_2:\text{N719}]/dt$ approaches zero, dye adsorption will be saturated. The dye adsorption reaction can be represented as follows.



According to the reaction of $aA + bB \rightarrow C$, the reaction rate can be expressed by $d[C]/dt = k[A]^a[B]^b$. Therefore, in eq 1, the reaction rate (r) can be represented by

$$r = \frac{d[\text{TiO}_2 : \text{N719}]}{dt} = k[\text{TiO}_2]^n[\text{N719}]^m \quad (2)$$

Where k is reaction constant and n and m represent reaction orders. $[\text{TiO}_2]$ represents the concentration of the adsorption sites in TiO₂

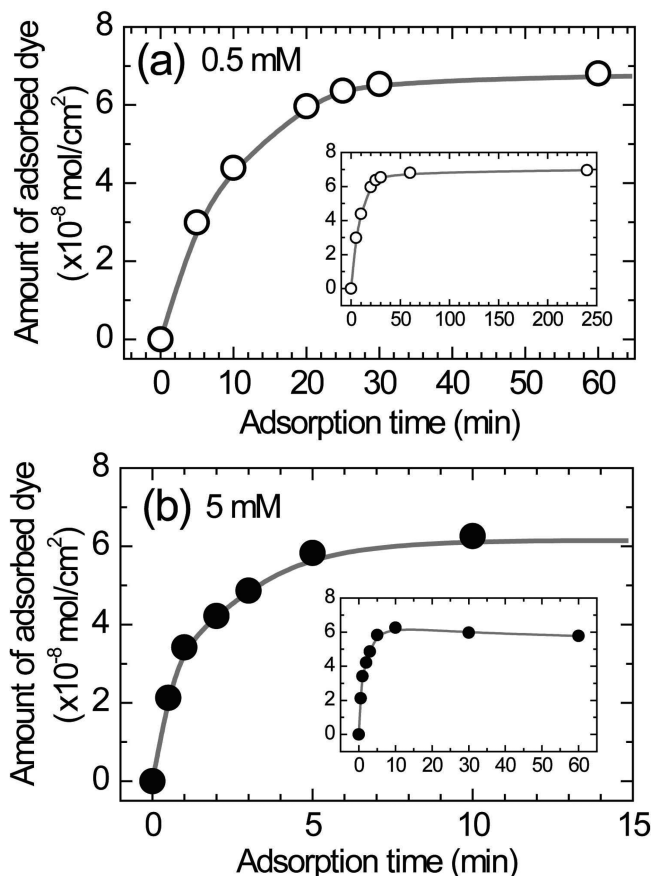


Figure 1. Amount of the adsorbed N719 dye from (a) 0.5 and (b) 5 mM solution as a function of adsorption time. TiO₂ film thickness was about 5 μm . Insets show change of amount of the adsorbed dye with adsorption time up to 240 min for 0.5 mM and 60 min for 5 mM.

film, which can be expressed as $[\text{TiO}_2:\text{N719}]_{\infty} - [\text{TiO}_2:\text{N719}]_t$, where $[\text{TiO}_2:\text{N719}]_{\infty}$ represents the saturated amount of the adsorbed dye and $[\text{TiO}_2:\text{N719}]_t$ is the adsorbed amount of dye at time t . $[\text{N719}]$ is the concentration of dye solution. Prior to attempting to estimate the reaction order and the reaction constant based on eq 2, the following factors should be first considered. We immersed the TiO₂ film with dimension of 0.5 cm² and thickness of about 5 μm into 10 mL of 5 mM N719 solution. In this case, the adsorption sites in TiO₂ film and number of N719 molecules can be evaluated as follows. The used TiO₂ film has weight of 0.5 mg and surface area of 65.62 m²/g as measured by BET method. Adsorption site for N719 was reported to be 1.95 per TiO₂ 1 nm².¹⁶ Therefore, the total N719 adsorption sites in the 0.5 cm² \times 5 μm TiO₂ film can be determined to be 6.40×10^{16} ($= 0.5 \text{ mg} \times 65.62 \text{ m}^2/\text{g} \times 1.95/\text{nm}^2$). The number of N719 dye molecules in 10 mL of 5 mM solution is 3.01×10^{19} ($= 0.005 \text{ mol/L} \times 0.01 \text{ L} \times 6.02 \times 10^{23} \text{ molecules/mol}$). Even in case that all of the adsorption sites in TiO₂ film are covered with dye molecules, the number of dye molecules will be decreased only by 0.2%, which indicates that the dye concentration remains almost unchanged. Similar is in case of 0.5 mM. In other words, the change of number of N719 dye molecules in the reaction is relatively negligible compared to the change of number of dye adsorption sites in TiO₂ film. Thus, the concentration of reactant dye, $[\text{N719}]$, can be set as constant because of almost no change during reaction. Equation 2 is therefore dealt with pseudo reaction^{17–20} and

Table 1. Comparison of Dye Coverage (θ) for First-Order Reaction Based on eq 7 in the Text^a

concentration of N719 dye (mM)	adsorption time t (min)	amount of adsorbed dye ($\times 10^{-8}$ mol/cm ²) [TiO ₂ :N719] _{t}	coverage		
			θ	$1 - \theta$	first-order $\ln(1 - \theta)$
0.5	0	0	0	1	0
	5	2.99	0.43	0.57	-0.562
	10	4.39	0.63	0.37	-0.994
	20	5.97	0.86	0.14	-1.966
	25	6.37	0.92	0.08	-2.526
	30	6.54	0.94	0.06	-2.818
	60	6.81	0.98	0.02	
	240	6.96	1	0	
5	0	0	0	1	0
	0.5	2.13	0.34	0.66	-0.416
	1	3.42	0.55	0.45	-0.799
	2	4.22	0.67	0.33	-1.109
	3	4.87	0.78	0.22	-1.514
	5	5.83	0.93	0.07	-2.659
	10	6.26	1	0	
	30	5.97	0.95	0.05	
	60	5.78	0.92	0.08	

^a The amount of the adsorbed dye was estimated by desorption from 0.1 M NaOH aqueous solution for 10 min.

can be rewritten as follows

$$r = \frac{d[\text{TiO}_2 : \text{N719}]}{dt} = - \frac{d([\text{TiO}_2 : \text{N719}]_{\infty} - [\text{TiO}_2 : \text{N719}]_t)}{dt} \quad (3)$$

$$r = k[\text{TiO}_2]^n[\text{N719}]^m = k'[\text{TiO}_2]^n = k'([\text{TiO}_2 : \text{N719}]_{\infty} - [\text{TiO}_2 : \text{N719}]_t)^n \quad (4)$$

where the reaction constant k' represents $k[\text{N719}]^m$. The saturated concentration of $[\text{TiO}_2 : \text{N719}]_{\infty}$ is determined when $d[\text{TiO}_2 : \text{N719}]/dt$ approaches zero, where time for $[\text{TiO}_2 : \text{N719}]_{\infty}$ is determined to be 60 min for 0.5 mM and 10 min for 5 mM because $d[\text{TiO}_2 : \text{N719}]/dt$ is 0.005 at 60 min for 0.5 mM and 0.035 at 10 min for 5 mM. By combining eq 3 with eq 4, we can obtain eq 5.

$$- \frac{d([\text{TiO}_2 : \text{N719}]_{\infty} - [\text{TiO}_2 : \text{N719}]_t)}{dt} = k'([\text{TiO}_2 : \text{N719}]_{\infty} - ([\text{TiO}_2 : \text{N719}]_t))^n \quad (5)$$

Since coverage (θ) is frequently used in the literature of adsorption, eq 5 can be alternatively expressed as eq 6 using θ ,

$$- \frac{d(1 - \theta)}{dt} = k'(1 - \theta)^n \quad (6)$$

where full coverage $[\text{TiO}_2 : \text{N719}]_{\infty} = 1$ and dye coverage $[\text{TiO}_2 : \text{N719}]_t = \theta$. The reaction order n can be obtained from eq 6 by simulation with zeroth- to higher order. We have tried to fit the data for zeroth-, first-, and second-order cases and found that the data follow first order. In case of the first-order reaction, the reaction rate is given by the following eq 7.

$$\ln(1 - \theta) = k't \quad (7)$$

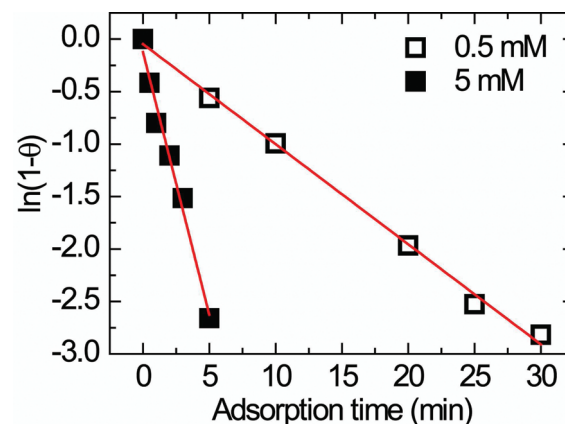


Figure 2. Dye coverage (θ) versus adsorption time for 0.5 mM (open square) and 5 mM (filled square) based on pseudo-first-order reaction, showing linear relationship between $\ln(1 - \theta)$ and time.

The plot using the data presented in Table 1 shows that $\ln(1 - \theta)$ is linearly proportional to adsorption time as can be seen in Figure 2, where both 0.5 and 5 mM cases follow linear relation with different slope k' . Therefore, the adsorption of ruthenium complex N719 dye on TiO₂ surface follows pseudo-first-order reaction, which is different from the second-order adsorption reaction of pure organic diazo dye on TiO₂ surface.²¹

When considering $r = k'[\text{TiO}_2]$, the reaction rate depends on the constant k' and the number of adsorption sites. Since we compared the adsorption behavior with the same dimension of TiO₂ film, the reaction rate is only dependent on the reaction constant k' . The reaction constant k' is determined to be 0.0942 min⁻¹ for 0.5 mM and 0.504 min⁻¹ for 5 mM from the slope at the first order reaction, which indicates that the adsorption

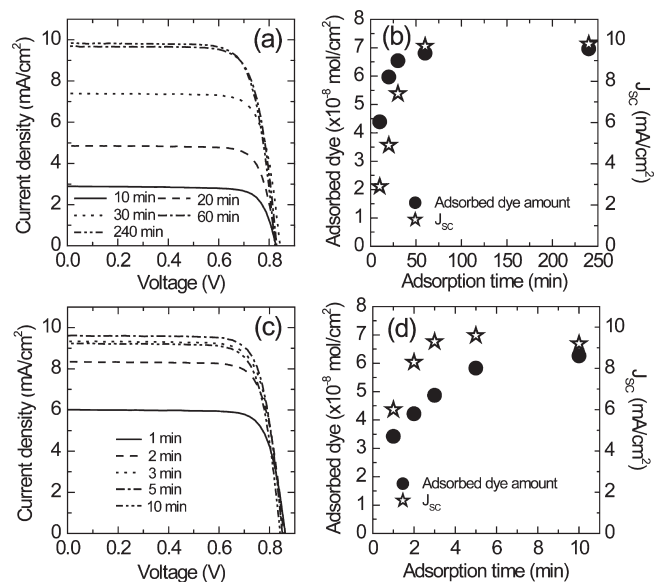


Figure 3. Photocurrent–voltage curves of dye-sensitized solar cells with different adsorption time for (a) 0.5 mM dye solution and (c) 5 mM dye solution. Comparison of photocurrent density (J_{SC}) and amount of the adsorbed dye as a function of adsorption time for (b) 0.5 mM dye solution and (d) 5 mM dye solution.

Table 2. Effects of Adsorption Time on Short-Circuit Photocurrent Density (J_{SC}), Open-Circuit Voltage (V_{OC}), Fill Factor (FF), and Overall Conversion Efficiency (η) of Dye-Sensitized Solar Cells

adsorption time (min)	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	η (%)	film thickness (μ m)
0.5 mM					
10	2.9	0.827	0.78	1.9	5.1
20	4.9	0.828	0.79	3.2	5.1
30	7.4	0.843	0.79	4.9	5.1
60	9.7	0.830	0.77	6.2	5.1
240	9.8	0.824	0.75	6.1	5.1
5 mM					
1	6.0	0.862	0.79	4.1	5.0
2	8.3	0.856	0.78	5.6	5.0
3	9.3	0.851	0.77	6.1	5.0
5	9.6	0.850	0.78	6.4	5.0
10	9.2	0.842	0.77	6.0	4.9

reaction in 5 mM is 5.35 times faster than that in 0.5 mM. As observed in Figure 1, dye adsorption is completed in about 60 min and about 10 min for 0.5 mM and 5 mM, respectively, which is indicative of 6 times faster in 5 mM than in 0.5 mM and is almost consistent with the difference in k' between 0.5 and 5 mM.

Since the amount of dye adsorbed in the given TiO₂ film is different with time, it is also interesting to investigate photovoltaic property depending on adsorption time. Panels a and c in Figure 3 show photocurrent–voltage curves depending on adsorption time for the case of 0.5 and 5 mM N719 dye solution, respectively, and the relevant photovoltaic parameters are listed

in Table 2. Photocurrent density increases with increasing adsorption time, while open-circuit voltage and fill factor are hardly influenced by adsorption time. When compared effect of adsorption time on photocurrent density and amount of the adsorbed dye in panels b and d in Figure 3, increase of photocurrent density with adsorption time is attributed to the increased amount of the adsorbed dye with time. Although the amount of the adsorbed dye is saturated at 10 min when using 5 mM N719 solution, maximum photocurrent density is obtained at 5 min. This is due to the fact that monolayer coverage is expected to be formed in 5 min and multilayer (due to dye agglomeration) is expected after 5 min, leading to higher dye loading for 10 min adsorption. Because the dye agglomerates have been known to be inactive for electron injection and shield the dye molecules in direct contact with TiO₂ from absorbing light,²² it is thus expected that the 10 min-adsorption exhibits lower photocurrent in spite of higher dye loading. For the case of low concentration of 0.5 mM, little change in dye loading with time after saturation at 60 min, indicating that multilayer adsorption does not occur at dye solution concentration as low as 0.5 mM. The best efficiency is obtained at 5 min adsorption from 5 mM solution and at 60 min adsorption from 0.5 mM, where photovoltaic performance is almost identical regardless of dye solution concentration but the only difference is in dye adsorption kinetics.

CONCLUSION

Dye adsorption kinetics was evaluated using 0.5 and 5 mM N719 solution. Dye uptake was 5 times faster at 5 mM. Ten times increase in the dye solution concentration did not lead to 10 times faster adsorption kinetics, which was explained by pseudo first order reaction and the reaction constant was found to be about 5 times larger for 5 mM than for 0.5 mM. In dye loading-performance relation, multilayer adsorption could happen at high dye solution concentration such as 5 mM, which might deteriorate photovoltaic performance. Although the amount of the adsorbed dye was saturated at 10 min when using 5 mM N719 solution, best performance was observed from the TiO₂ film immersed in dye solution for 5 min. For low dye solution concentration such as 0.5 mM, multilayer adsorption was hardly expected because of little change in dye loading with time even after saturation in dye loading. Except for the adsorption kinetics, the optimal efficiency was similar regardless of dye solution concentration.

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