Influence of Measurement Conditions on Electron Diffusion in Nanoporous TiO₂ Films: Effects of Bias Light and Dye Adsorption

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Electron diffusion coefficients in bare and dye-adsorbed nanoporous TiO₂ films filled with electrolytes are estimated using a pulsed laser in the presence and absence of a continuous light irradiation. It is found that the orders of estimated values of the diffusion coefficients are in agreement regardless of the existence of the bias light. Using a UV pulse measurements without bias light, influence of the dye adsorption on electron transport is found in the increase of the electron diffusion coefficient in the films. The measurement without bias light seems to be able to provide a convenient method to compare the electron transport properties among various nanoporous TiO₂ films and to study the influence of surface adsorption on electron transport in the films.

Introduction

Electron transport mechanism in nanoporous TiO₂ films immersed in electrolytes has been studied especially along with the development of dye-sensitized solar cells (DSC).[1−17] This is because the electron transport in the films is one of the most important factors affecting the solar cell energy conversion efficiency. The nanoporous films are typically prepared from nanosized TiO₂ particles followed by annealing. DSCs are made of a dye-adsorbed nanoporous film filled with electrolytes. In DSC, electrons in the films are surrounded by high concentration of cations derived from the salts dissolved as iodide/polyiodide electrolytes. This condition probably results in the absence of large electric filed gradient in the film.[3,11] Hence, the electron transport has been described mainly with diffusion.

To measure the electron transport in nanoporous films, several methods have been proposed. Solbrant et al. employed a pulsed UV laser to generate electrons in a shallow depth from the surface of TiO₂ films and measured the transient time of the electrons to reach the other side of the films.[4] Diffusion of electrons was indicated from the observations that the current transient time was proportional to the square of the film thicknesses. The same group also measured dye-adsorbed TiO₂ films with a pulsed laser (Nd:YAG, 532 nm) with various pulse intensities, showing that the electron diffusion coefficient (*D*) increased with the intensity.[5] These measurements used a constant *D* to interpret the current transients. One concern of these measurements is that the laser pulse disturbs electron density in the conduction band largely from the dark steady condition, and electron diffusion coefficients will change continually respect to time and position while the pulse-induced current goes back to zero. An approach to handle this is to solve the diffusion equation including the electron density dependent *D*.[2] However, solving the equation is not trivial since the *D* depends nonlinearly on the electron density. Modeling of

nonthermalized electrons may be also required, but the equation may not be solved analytically.[9]

Another approach is using a sinusoidal modulated light[2,3,6,12] or a pulsed laser[9,13,14] superimposed on a continuous light (bias light) irradiation. These methods allow the measurement under nearly steady conditions by using the much smaller intensity of the modulated light than that of the bias light. Then, *D* may be treated as a constant against the excess electrons by the modulated light, and the *D* depends only on the intensity of bias light. In terms of the probe light modulation method, it has been reported that current transient induced by a pulse is related with inverse Fourier transform of the results obtained from sinusoidal modulated light.[9] Duffy et al. reported that agreements were obtained between the measurements performed by pulse and sinusoidal modulated lights with bias light.[14]

The intensity dependence of electron diffusion, which was carefully measured by changing the bias light intensity, showed the power law dependence on the light intensity.[6] This observation was interpreted with intraband charge trap sites whose energy level has an exponential[7,9] or Gaussian distributions.[10] On the basis of the model, electrons diffuse through the thousands of trapping and detrapping, causing much slower diffusion than that in bulk crystalline TiO₂.[9] This model also indicates that *D* has a deviation caused by the distribution of electron transit times even under steady condition.

On the basis of these observations and models, applying bias light seems to provide a measurement condition which makes it simple to apply the measured results to the models. The influence of the presence of bias light on electron diffusion measurements was reported by Kopidakis et al.,[13] who showed the unexplainable 2 orders of magnitude difference between the measurements with and without bias light. On the other hand, some measurements performed without bias light have shown rough agreements with that performed under bias light.[4,5,15,16] Table 1 summarizes the experimental conditions used by several groups found in the literature. As it can be seen, various conditions have been employed. Influences of the modulation method and light absorption coefficient on the analysis were

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TABLE 1: Summery of Previously Reported Experimental Conditions for Electron Diffusion Measurements, and Conditions Used in This Work[a]

| reported by | modulated light | | bias light/nm | dye adsorption | D estimated by | year |
	type	λ/nm				
Cao et al.[2]	sinusoidal	512	512	yes	fitting	1994
	pulse	512	N/A	yes	fitting	
Solbrand et al.[4]	pulse	308	N/A	no	$D = w^2/6t$	1997
Dloczik et al.[6]	sinusoidal	470	tungsten	yes	fitting	1997
Solbrand et al.[5]	pulse	460	N/A	yes	fitting	1999
Kopidakis et al.[13]	pulse	670	tungsten	yes	$D = w^2/4t$	2000
	pulse	670	N/A	yes		
Duffy et al.[14]	pulse	532	543	yes	fitting	2000
this work	pulse	355	N/A	no	$D = w^2/6t$	
	pulse	532	632	yes	$D = w^2/2.35t$	
	pulse	355	N/A	yes	$D = w^2/6t$	

[a] Key: w, TiO$_2$ electrode thickness; t, characteristic time constant of current response.

examined before.[9,14] However, the influence of existence of bias light has not been paid much attention. In this article, we measure pulsed laser-induced current transients from the same nanoporous TiO$_2$ electrodes both in the presence and in the absence of bias light. The conditions examined here are also shown in Table 1. Influence of the adsorbed dye on the films on electron transport will be briefly mentioned.

Experiments

Nanoporous TiO$_2$ films are prepared from a colloidal suspension of TiO$_2$ nanoparticles (P25, Nippon Aerogel) by dropping on a transparent conductive oxide (TCO) glass (Nippon Sheet Glass, SnO$_2$:F, 8 ohm/sq) with using doctor-blade technique. The films were annealed at 450 °C for 30 min in air. The thickness of the TiO$_2$ films was between 3 and 9 μm, as measured by a profiler. For the sensitization study, heated TiO$_2$ films at around 110 °C were immersed in an acetonitrile/2-methyl-2-propanol (1:1) solution containing 0.5 mM Ru-dye (Bu$_4$N)$_2$[Ru(Hdcbpy)$_2$(NCS)$_2$] (known as N719, Solaronix) for at least 24 h at room temperature, and subsequently, the films were rinsed by acetonitrile. DSCs were prepared with an electrolyte consisting of 0.1 M LiI, 0.05 M I$_2$, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide, and 0.5 M 4-*tert*-butylpyridine in methoxyacetonitrile and a Pt-sputtered TCO glass.

Electron diffusion coefficients (D) of bare TiO$_2$ films were estimated as described elsewhere.[4,15] In short, a TiO$_2$ film was attached to a window of a quartz cell filled with an electrolyte containing 0.7 M LiClO$_4$ in ethanol. Then, the film was irradiated by a short UV pulse (flash-pumped Nd:YAG, 7 ns, λ = 355 nm) through the electrolyte. An aperture was located in from of the film, selecting the spot size to be 0.09 cm^2. A Pt wire was used as a counter electrode. In this measurement, it was assumed that holes generated by the UV pulse were filled by electrons from the ethanol in much shorter time than the transit time so that only exited electrons are left in the films during the transit.[15] D were estimated with the current transient peak time (t) and the film thickness (w) by $D = w^2/6t$.[18] Electron density was estimated by integrating the corresponding current transient. This measurement was also applied to dye-adsorbed TiO$_2$ films with the same setup. For this case, bleaching of the dye by the UV laser was not observed during the measurements.

Under bias light from a HeNe laser (Melles Griot, λ = 632.8 nm), D in dye-adsorbed TiO$_2$ films were measured from current transients induced by a short pulsed laser (Nd:YAG, 7 ns. 532 nm) using DSC. Theory[9] and setup[17] for this measurement are described in detail elsewhere. The laser pulse was irradiated from the Pt counter electrode side of the DSC. Note that the Pt
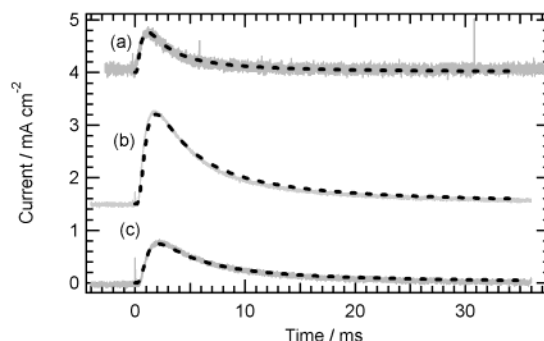

Figure 1. Pulsed laser-induced current transients from TiO$_2$ films in dye-sensitizes solar cell and immersed in 0.7 M of LiClO$_4$ in ethanol. The transient for part a was obtained from DSC having a 8.5 μm-thick TiO$_2$ film by a green pulse under bias light, that for part b was from a 6.2 μm-thick bare TiO$_2$ by a UV pulse without bias light, and that for part c was from a 7.3 μm-thick dyed TiO$_2$ film by a UV pulse without bias light. Background current was 6.7 mA/cm^2 for transients (in part a) and zero for parts b and c. Dashed lines are calculated transients from an analytical solution of trap-free diffusion equation with diffusion coefficients of 10 (a), 3.2 (b), and (c) 4.0 × 10^{-5} cm^2 s^{-1}.

layer is thin enough so that partial intensity of the pulse can transmit though the electrode. Since the absorbance of the adsorbed dye at the wavelength of bias light is low, nearly homogeneous electron excitation along the film thickness is expected. Current transients were measured through a current preamplifier (Sanford Research Systems, SR570) or a potentiostat (Toho Technical Research 2001) and recorded on an oscilloscope. The intensity of the HeNe laser and the YAG laser was changed by a set of ND filters. In comparison to the lowest intensity of HeNe laser used here, the densities of the excess electrons induced by the pulsed laser were estimated to be about one tenth of that by the bias light. Electron diffusion coefficients were estimated with a time constant of current transient decay (τ_C) and the TiO$_2$ film thickness by $D \sim w^2/2.35\tau_C$.[9]

Results and Discussion

Electron Diffusion Coefficients Measured in the Presence and Absence of Bias Light. Figure 1 shows typical current transients induced by a laser pulse both in the presence and absence of bias light. Electron diffusion coefficients in the nanoporous TiO$_2$ films derived from the transients are summarized in Figure 2. The D values of the bare TiO$_2$ films were borrowed from our previous results.[15] As a reference, data reported by Kopidakis et al.[13] are also included in Figure 2. We plotted D vs mean electron density in the film (top axis)
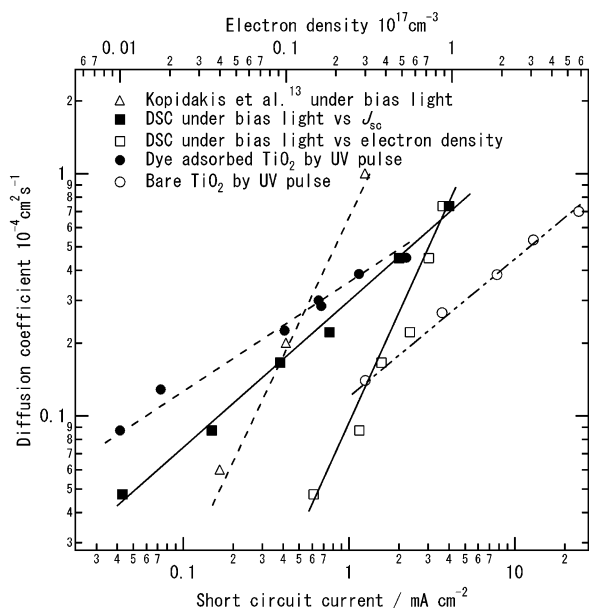
Figure 2. Diffusion coefficients of electrons in bare and dyed TiO_2 films measured without bias light as a function of mean electron density (top axis) and measured in DSC measured under bias light as a function of J_{sc} (bottom axis). The open rectangular represents the diffusion coefficients in DSC under bias light, when the electron density (n) was estimated by using $n = J_{sc}\tau/qw$ (top axis).

Figure 3. Electron diffusion coefficients in DSC having three different TiO_2 thicknesses (rectangular, 8.5 μm; circle, 6.1 μm; triangle, 4.3 μm) Measurements were performed with optical bias. Since the short circuit current was proportional to the thickness, bottom axis was obtained from the short-circuit currents divided by the thickness of the films to represent the electron density in the films.

for bare and dye-adsorbed TiO_2 films measured using a UV pulse without bias light, and D vs short-circuit current (J_{sc}, bottom axis) in DSC measured with bias light. To estimate electron density in the films for DSC, J_{sc}, and electron transient time (τ) may be used with $J_{sc}\tau/qw$, where q is the electron charge.[13] On the basis of this estimation, the range of bottom axis was chosen to roughly agree with the range of the top axis. The plot of D in DSC vs electron density, estimated from $J_{sc}\tau/qw$, was also included in Figure 2.[19] In comparison between the D in the dyed files measured by UV and green pulses, the values measured here were found in the same order. Since both measurements were performed with similar conditions, i.e., with dye adsorption and in the same concentration of cations, this agreement suggests that both methods can describe the electron transport similarly.[20]

When electrons transport though the event of trapping/detrapping, the measured diffusion is the average from the electrons that had different transport experiences. The bias light is supposed to provide uniform electron distribution in the films so that the electrons would experience a similar condition during the transport. This would reduce the deviation of the averaged diffusion coefficients. The agreement observed here regardless of the existence of bias light implies that the averages of the electron diffusion coefficients were similar but the deviation, which is not derived here, from the averaged values would depend more on the bias light. The agreements of the averaged values here can be interpreted with several reasons.

Diffusion Coefficient Obtained from Various Electrode Thicknesses. In DSC, J_{sc} is mainly determined by the electron concentration gradient at the TiO_2/TCO interface.[21] Then, the electrons in the gradient may not be described adequately with one effective diffusion coefficient due to the gradient of Fermi level. Note that D depends on the Fermi level in the TiO_2 films. Under bias light, we measured D with different thickness films between 4.3 and 8.5 μm. As shown in Figure 3, the D increased with the film thickness when the D was plotted with the values obtained by J_{sc} divided by the film thickness. Here, the J_{sc} was
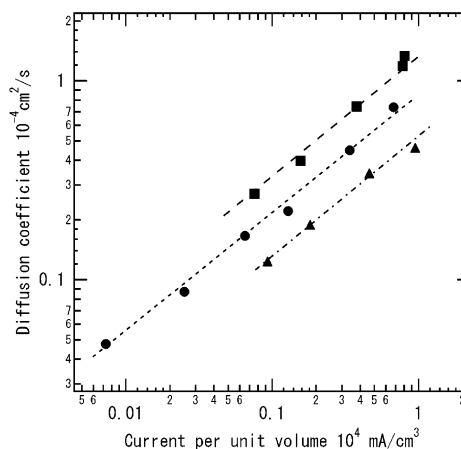
nearly proportional to the film thickness, suggesting that the relatively uniform photogenerated electron density in the films was obtained by the bias light. Park et al. has also reported that the D was increased with the film thickness.[22] Although they concluded that the increase was in experimental error, this coincidence implies that even under bias light, Fermi level gradient in the films caused by the gradient of electron density influences the current transient times.[23] And this difference from the ideal condition presumably obtained by bias light may make the difference of these films' condition small between with and without bias light measurements.

Trap-Free Diffusion Model and Measurements without Bias Light. As mentioned above, a constant D was not expected to be able to describe the current transients induced by a large intensity pulse, since the electrons travel from one side to the other side of the film, which may have large different trap filling conditions along the film thickness. To explain the agreement observed in Figure 2, the results of UV pulse measurements may be interpreted with the time scale for averaging the electron diffusion coefficients. In a short period of time after the pulse irradiation, electrons are probably not thermalized yet. Then, some electrons are able to transport without trapping in the period.[9] This was also demonstrated by Monte Carlo simulations performed by Cass et al.[24] With increasing the time scale, these electrons would interact with many traps, and then the deviation of D from all electrons will become small. In other words, just after the UV pulse irradiation, some electrons could transport much faster than the thermalized electrons and fill the traps located far from the place electrons generated. As can be seen in Figure 1, the increase of the current started in microseconds while we discussed current transients on a millisecond scale. This shows that many electrons reached the TCO side in less than millisecond after the UV pulse irradiation. This fact would result that the measured electrons, around the time when the current peak appeared, have transported in the films that have thermalized electrons with similar electron density through the film.

If this were the case, the transients would be fitted by a solution of diffusion equation with a constant D. Actually, in ref 5, the transients measured without bias light were fitted well for some period of time. Here, we also fitted the transients in Figure 1 with an analytical solution of diffusion equation

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(boundary conditions and equations used for the fitting are explained in the Appendix). The all transients were fitted well regardless of the bias light and dye adsorption. This result also suggests that the transients obtained without bias light are reasonably described by a constant D. During the transient, electron density in the film is decreasing as the electrons flowing out. Then, the D at the long tail should not be the same as the D just after the pulse irradiation. When the decay of the current transient (b) in Figure 1 is fitted for the time period of 30 ms with an exponential function and D is obtained with $w^2/2.35\tau$, D differs from that obtained from the peak time by 3%.[25] This difference shows how well a constant D can approximate the actual D, which is changing during the transient.

Influence of Dye Adsorption on D. In comparison between D measured in bare and dyed TiO_2 by a UV pulse in Figure 2, the D values in dye-adsorbed TiO_2 films were larger than those in bare TiO_2 films under the range of the pulse intensity used here. The D and its slope in the double logarithmic plot have been interpreted with the charge trap density and distribution. The results observed here imply that the dye adsorption changed the condition of surface charge traps.[26] In addition to this, it has been reported that chemical environments can induce the change of charge-trap condition,[27,28] and the dyes would influence the environments. We also found that the increase of D by dye adsorption scaled with the surface area of nanoporous films.[29] From the viewpoint of the measurement method, employing UV pulse without bias light makes it easy to compare the influence of chemical surroundings and absorptions on D in TiO_2, e.g., species and concentration of cations,[30] and different dye adsorptions, while using bias light requires redox mediators and probably dye sensitization, which makes it difficult to rule out each influence. The simple measurement condition for UV pulse measurements is one advantage in compassion to optical bias measurements.

Measurements on Different Samples. We reported that electron diffusion coefficients depend on TiO_2 nanoparticle size.[17] In the report, we measured the D in DSC with bias light. D in the identical films without dye adsorption was also measured by a UV pulse without bias light with the same setup described in this paper (data not shown). In the both measurements, we observed D in the same order and the same tendency that the D increased with the increase of the TiO_2 particle size. This agreement between the two measurements supports the point that both methods are applicable to compare these electron transport properties in various nanoporous electrodes.[31]

Conclusions

Pulsed laser-induced current transients from nanoporous TiO_2 films were measured both in the presence and in the absence of bias light. Electron diffusion coefficients (D) were estimated by using a constant D in diffusion equation for each current transient. Regardless of the methods, the derived D values from the transients were found in the same order and dependency on electron density. This suggests that the both methods can be used to compare electron transport properties among different nanoporous films. The agreement of the measured values may be interpreted with that the averaged diffusion coefficients are close each other due to similar spatial electron density distributions with similar averaging times, while the existence of the bias light may influence more the deviation of the D. Influence of dye adsorption on electron transport was found in the increase of the electron diffusion coefficient, which may be explained as due to the change of film-surface trap-state distribution by the adsorption.

Appendix

A simple model to describe electrons in DSC may be presented as

$$\frac{\partial n(x,t)}{\partial t} = D_{app}\frac{\partial^2 n(x,t)}{\partial x^2} + G(x,t) - R(x,t) \qquad (A1)$$

where n is electron density, x is the position from TCO, G is the electron generation term, R is the recombination term, and D_{app} is the apparent diffusion coefficient, which includes the influence of charge traps. This equation becomes a simple diffusion equation when a short pulse is applied so that G can be omitted and electrolytes are chosen giving a long charge recombination lifetime allowing one to neglect R. For the film having a thickness of L, the initial condition describing electron density just after a pulse irradiation may be described by a δ function at the outermost layer at $x = L$, $\delta(x - L)$. Boundary condition may be chosen that electrons at $x = L$ are reflected, i.e., $dn(L,t)/dx = 0$, and electrons at $x = 0$ are immediately removed to the TCO so that $n(0,t) = 0$. This boundary condition can be satisfied by setting a delta function of negative charge at $x = -L$ in the initial condition. Then, $n(x,t)$ can be written by

$$n(x,t) = \frac{N}{\sqrt{4\pi Dt}}\exp\left(\frac{-(x-L)^2}{4Dt}\right) + \frac{-N}{\sqrt{4\pi Dt}}\exp\left(\frac{-(x+L)^2}{4Dt}\right)$$
$$(A2)$$

where the half of N is the initial electron density. Diffusion current at $x = 0$ is obtained by

$$J = qD\frac{dn(x,t)}{dx}\bigg|_{x=0} \qquad (A3)$$

where q is the elementary charge, and then

$$J = \frac{qNL}{2\sqrt{\pi Dt^3}}\exp\left(-\frac{L^2}{4Dt}\right) \qquad (A4)$$

which is the same as that found in ref 4. When the decay of this current transient is fitted by a single-exponential function $\exp(-t/\tau)$, the fitted τ is related to D and L by $\tau \approx L^2/(2.35D)$. Current transients in Figure 1 were fitted with eq A4.

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(18) In refs 15, 16, and 30, D was derived using current transient peak time (t) by $D = w^2/2t$, where we thought the current is proportional to electron density at $x = 0$. If all electrons move by diffusion, then the current is proportional to electron density gradient at TCO/TiO$_2$ interface and $D = w^2/6t$. However, uncertainty still remains how the potential drop at the interface influences the concentration gradient and current transients.

(19) The D in DSC vs electron density was plotted to compare with the data in ref 13. The difference of the slope from the D vs J_{sc} and the calculated electron density was probably caused from the method of the estimation of the electron density. To estimate the electron density in the films under bias light irradiation, we have measured the short circuit current decay after the bias light was turned off and estimated the density from the integration of the current decay. This was repeated with various bias light intensities and film thicknesses. When the D in DSC was plotted with the electron density estimated from the current decay, the values and slope were more comparable with D in dye-adsorbed films measured by UV pulse. The data still seem to contain error due to the relatively large noise in the tail of the current decays. Thus, at this moment, we used the current decay data to check the order of the electron density under bias light irradiation. Since the electron density by UV pulse and J_{sc} by bias light are proportional to the light intensity, in this article, we mainly compared the D vs n for UV pulse and D vs and J_{sc} for optical bias measurement.

(20) Diffusion coefficients in the electrolyte filled nanoporous films can be interpreted with ambipolar diffusion, where the measured diffusion coefficients are related with diffusion coefficients and concentrations of negative and positive charges (see refs 13, 15, and 30). For the condition of the large concentration difference between the charges, the measured diffusion coefficient is approximated to the diffusion coefficients of minority carriers. Since the electron density examined here is a few orders of magnitude lower than that of cations, we assume the measured diffusion coefficients represents the electron diffusion coefficients.

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(25) We would like to note that the fitting results in Figure 1 do not guarantee that measurements without bias light can always provide comparable results with that with bias light. For example, if a UV pulse were applied on very thick films, the spatial distribution of electron density would be too large to be approximated by a constant D. Another nonapplicable case would be when the electron density in the film is too high comparing with cation concentration. For the case, D is more sensitive to the electron density so that rather small spatial distribution of electron density can disturb the current transients largely from simple diffusion limited transients. Distorted transients found in refs 4, 5, and 15 are probably explained by the reasons noted above.

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(31) The electron diffusion length in the DSC under working condition is important aspect to measure. To estimate the accurate value, it is probably required to measure both D and electron recombination lifetime in DSC at the same circuit condition. The derived diffusion coefficients without bias light and dye adsorption can be used for TiO$_2$ film assessments in comparison but not for accurate values in DSC.