

# Laser-Induced Photovoltage Transient Studies on Nanoporous TiO<sub>2</sub> Electrodes

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At open circuit, pulsed-laser-induced photovoltage transients of nanoporous TiO<sub>2</sub> electrodes filled with an electrolyte are studied using various pulse intensities and electrode thicknesses. The transients are interpreted using the electron diffusion in the electrodes. This is compared to the studies of electron transport, which was performed using photocurrent transients at short circuit. A similar light intensity dependence of electron diffusion is found from the photovoltage transients. Electron diffusion coefficients are estimated by fitting of the photovoltage transients with the solution obtained by solving a diffusion equation with a simple boundary condition. The fitted values of the electron diffusion coefficients at open circuit are lower than those derived from the photocurrent transients at short circuit. The difference suggests that Fermi level gradient, caused by nonuniform electron distribution in the electrode under short-circuit conditions, has significant influence on the electron transport. Observed photovoltages are plotted with corresponding electron densities in electrodes, showing logarithmic relationship. Difference and advantages of the photovoltage transient measurements in comparison to short-circuit transient measurements are discussed.

## Introduction

Nanoporous metal oxide electrodes have been applied to many applications with taking advantage of their nanosize, such as their high surface area. One of the applications is dye-sensitized solar cell (DSC), which has been paid a lot of interest because of the high energy conversion efficiency and unique structures.<sup>1</sup> Understanding electron transport in the nanoporous electrodes is important for further improvement of the functionalities of these applications. Large efforts have been made along this direction by many groups.<sup>2–20</sup> For the solar cells, nanoporous electrodes are typically prepared from nanoparticles on a transparent conductive oxide (TCO) glass followed by annealing. The porosity of the resulting electrodes ranges between 40 and 60%. The electron transport in the electrodes immersed in electrolytes has been considered with diffusion because cations in the solution are likely to screen the electrons in the electrodes.<sup>6,9</sup> The electron diffusion coefficients in the electrodes have been derived from experimental results, showing much slower values than that in a bulk crystal, and strong light intensity dependence.<sup>3–5</sup> These observations have been mainly interpreted as due to intraband charge traps that capture and release electrons during the transport.<sup>7,8,10</sup> Thus, the measured diffusion coefficients can be considered as apparent diffusion coefficients which include the trapped time during the transport.

To study electron transport in nanoporous metal oxide electrodes immersed in an electrolyte, several techniques have been employed, such as intensity modulated photocurrent spectroscopy (IMPS),<sup>3,5,6,8</sup> intensity modulated photovoltage spectroscopy (IMVS),<sup>20</sup> and pulsed-laser-induced photocurrent transient measurements.<sup>4,10–12,14</sup> To derive the electron diffusion coefficients, measured current transients were analyzed with solving a diffusion equation with boundary conditions. However, at short circuit, the condition of the TCO/metal oxide interface, for example, electric field gradient, has not been fully understood

yet.<sup>9,13,19</sup> Then, it has been assumed that there is no boundary at the interface from the viewpoint of electron transport;<sup>4</sup> the TCO behaves as an ideal sink so that the excess electron density at the interface is zero<sup>3,10</sup> or activation energy is involved at the interface.<sup>5</sup> Thus, the analysis of measured photocurrents has been restricted by the uncertainty of the boundary condition at the TCO/TiO<sub>2</sub> interface. In addition to these, current transient measurements can be influenced by RC time constant<sup>5,6</sup> or potential barrier at the interface.<sup>21</sup> The origin of the capacitance that appeared in the experimental data is under debate,<sup>22</sup> complicating the analysis of the current transients further.

To study the electron transport and the influence of interface without suffering from these issues, measurements of open-circuit voltage transients would provide the information relating only the electron transport in the electrodes. This is because the electrons do not have to travel across the interface and the transit time in the electrodes can be measured from the voltage transients, which relate with the number of electrons reached to the interface. Photovoltage transients of nanoporous TiO<sub>2</sub> were measured previously in dry conditions.<sup>17</sup> However, few studies have measured electron transport in electrolyte filled TiO<sub>2</sub> electrodes from open-circuit voltage transients. Cations in electrolyte solutions can be the countercharges of electrons in the electrode and, consequently, the electron transport dynamics differs from that in a vacuum or in gas.<sup>12,15,16</sup> The aim of the paper is to study the electron transport in electrolyte filled nanoporous TiO<sub>2</sub> and the influence of circuit condition on the electron transport, by means of photovoltage transient. In addition to these, charge-trap densities in the electrodes are also estimated from the photovoltage and corresponding electron density in the electrodes.

**Diffusion Equation.** Electron transport in nanoporous electrodes under light irradiation has been interpreted with time-dependent diffusion equation, which is given by

$$\frac{\partial n(x,t)}{\partial t} = D \frac{\partial^2 n(x,t)}{\partial x^2} + G(x,t) - R(x,t) \quad (1)$$

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where  $n$  is the electron density as a function of position  $x$  and time  $t$ ,  $D$  is the electron diffusion coefficient, and  $G$  and  $R$  are the photoelectron generation and recombination rate, respectively.<sup>5</sup> Experiments to study electron transport have been performed by using a large intensity pulse<sup>4</sup> or by using either a small intensity pulse<sup>10</sup> or sinusoidal modulated light<sup>5</sup> superimposed on large intensity steady light. As it has been reported, the  $D$  depends on the electron density in the electrodes.<sup>3,5,12</sup> Large intensity pulse measurements generate large changes of the electron density in the electrode over a period of time. Then, the diffusion coefficient derived from a large intensity pulse could be considered as an average of diffusion coefficients with relatively large deviation. Small perturbation measurements would allow electrons to transport under nearly steady condition. This would result in the derived  $D$  having smaller deviation. In this paper, we assume that trap-free diffusion equation can be used to analyze both the short-circuit current and photovoltage transients.<sup>23</sup> The influence of bias light will be addressed in a later section.

To solve the diffusion equation, a boundary condition should be set. When photovoltage transient is induced by a short UV pulse and measured at open circuit, this condition allows us to neglect the generation term in eq 1 and to set a simple boundary condition, that is, electron flow at the both ends of the electrode is zero. By using an ethanol without redox couples, electron recombination lifetime is in the time scale of second,<sup>14</sup> which is longer than the transient time observed here. Thus, the recombination term in eq 1 was also dropped for the sake of simplicity.<sup>24</sup> We can consider that electrons travel in one-dimensional space by using much larger laser-spot size than the electrode thickness. Then, the one-dimensional diffusion equation with the boundary condition and an initial condition can be solved analytically. Using delta function for the initial electron distribution, generated by a UV laser pulse at the outermost layer of TiO<sub>2</sub> electrodes, as the initial condition, the electron density can be described as

$$n(x,t) = \sum_{m=0}^{\infty} \frac{N}{2\sqrt{4\pi tD}} \left\{ \exp\left(\frac{-(x - (1 + 2m)L)^2}{4tD}\right) + \exp\left(\frac{-(x + (1 + 2m)L)^2}{4tD}\right) \right\} \quad (2)$$

where  $L$  is the electrode thickness and  $N$  is the number of photogenerated electrons. This solution was obtained by setting image charges at  $-(1 + 2m)L$  and  $(1 + 2m)L$ , where  $m$  is an integer, except at  $x = L$ , where real electrons exist. This condition satisfies the boundary condition of  $dn/dx = 0$  at  $x = 0$  and  $L$ . Then, the photovoltage may be obtained with the electron density at the TCO/electrode interface, which is at  $x = 0$ , by

$$V_{oc}(t) \approx k_B T \alpha \log(n(0,t)/n_0) \quad (3)$$

where  $k_B$  is the Boltzman constant,  $T$  is the temperature,  $n_0$  is the steady-state electron density, and  $\alpha$  is a constant. The constant  $\alpha$  is related with the trap site distribution. If there are no intraband traps,  $\alpha$  is 1. Then, electron diffusion coefficient can be estimated by fitting the measured photovoltage transients with eq 3. Since the time scale for the transient measurements here is less than 100 ms, and the order of  $D$  is less than  $10^{-4}$  cm<sup>2</sup> s<sup>-1</sup>,  $m = 8$  was used for eq 2 to reduce calculation time.

## Experimental Sections

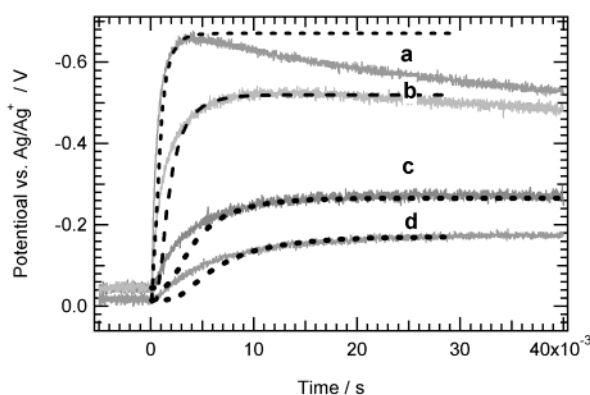
Nanoporous TiO<sub>2</sub> electrodes were prepared by dropping the colloidal suspensions of TiO<sub>2</sub> nanoparticles (P25,  $d = 21$  nm, Nippon Aerogel, and Nanoxide-T,  $d = 18$  nm, Solaronix) on transparent conductive glasses (Nippon Sheet Glass, SnO<sub>2</sub>:F, 8 ohm/sq) with a glass rod and adhesive tapes as a spacer. The resulting electrodes were annealed at 450 °C in air for 30 min. The thickness of the electrodes ranged between 2 and 10 μm as measured by a profiler. The porosity of the electrode was estimated to be ca. 60% by nitrogen absorption-desorption measurements. An electrolyte solution was prepared from 0.7 M of LiClO<sub>4</sub> in ethanol. In the measurements, the ethanol acts as a hole scavenger.

To measure photovoltage transients, the electrodes were attached with O-ring having area of 0.65 cm<sup>2</sup> to a quartz cell filled by the electrolyte.<sup>25</sup> A Pt wire and Ag/Ag<sup>+</sup> electrode were used as a counter and a reference electrode, respectively. A flash-pumped Nd:YAG laser (Quanta-Ray, fwhm = 7 ns,  $\lambda = 355$  nm) was employed as a UV pulse source. An aperture was placed in front of the cell, selecting the pulse area to be 0.12 cm<sup>2</sup>. The intensity of the pulses was controlled by a set of optical filters. A mechanical shutter synchronized with the laser's repetition frequency was used to select the number of applied pulses. Photovoltage was induced by applying a pulse to the electrodes through the electrolyte. In the measurements, we assume that photogenerated holes will be filled by ethanol just after the laser irradiation, and only electrons will transport in the electrodes.<sup>4,14</sup> The voltage transient was monitored through a potentiostat (Toho Technical Research 2001) by a digital oscilloscope. Measurements were repeated several times at each condition after a few to 10 min resting time at the potential of +200 mV versus Ag/Ag<sup>+</sup>. Photocurrent transients at short circuit were measured by the same setup using the potentiostat or a current amplifier (Stanford Research Systems, SR570). Electron diffusion coefficient from the transients was derived from  $D = L^2/6t$ , where  $t$  is the time giving maximum current.<sup>14,18</sup> In the analysis for current transient, the same diffusion equation, eq 1, and assumptions used for the voltage transient analysis were used, except for the boundary condition at  $x = 0$  for  $n(0,t) = 0$  at short circuit. The electron density in the electrodes was estimated by numerical integration of the corresponding current transients.

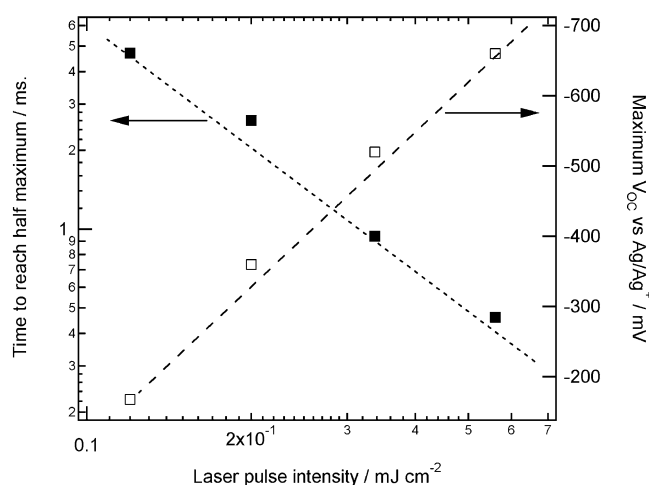
## Results and Discussion

**Photovoltage Transients and Electron Diffusion.** Figure 1 shows the measured photovoltage transients from a 6.0-μm-thick electrode prepared from P25 with various laser pulse intensities. Here, we defined a transit time ( $\tau_{TR}$ ) to reach half of the maximum  $V_{oc}$ :  $V(\tau_{TR}) = V_{oc,max}/2$ . As increasing the pulse intensity, the maximum photovoltage was increased with decreasing  $\tau_{TR}$ . Figure 2 shows the  $V_{oc,max}$  and  $\tau_{TR}$  obtained from Figure 1 as a function of the pulse intensity. This observation was consistent with the results observed in photocurrent transient measurements at short circuit.<sup>3,5,12</sup> Thus, the decrease of  $\tau_{TR}$  can be interpreted with that the electron diffusion coefficient was increased with the increase of electron density in the electrodes. The plateau of the voltage in Figure 1 suggests that the electrons are distributed uniformly in the electrode and have a longer time constant for the charge recombination compared with the transit time. As increasing pulse intensity, the decays of the photovoltage after reaching the peak  $V_{oc}$  were observed.

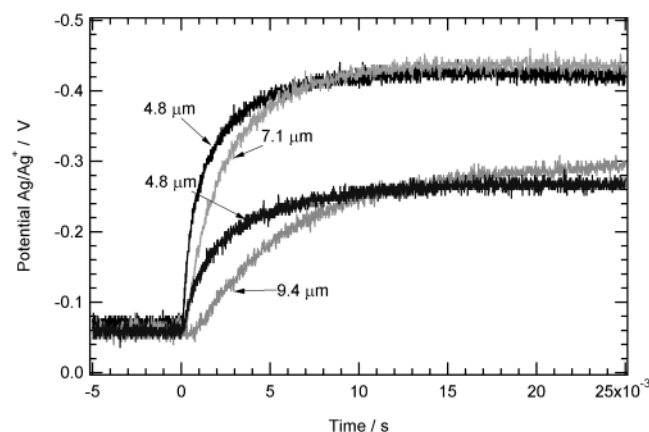
Figure 3 shows photovoltage transients from the electrodes having different thicknesses. The similar maximum photovoltages from different thickness electrodes were observed when



**Figure 1.** Measured photovoltage transients from a 6- $\mu\text{m}$ -thick  $\text{TiO}_2$  nanoporous electrode consisting of 21-nm size of  $\text{TiO}_2$  particles (P25) with various UV laser pulse intensities. The electrolyte was 0.7 M  $\text{LiClO}_4$  in ethanol. The pulse energy densities were a, 0.56; b, 0.33; c, 0.20; and d, 0.12  $\text{mJ}/\text{cm}^2$ . Dashed lines are obtained from an analytical solution of time-dependent diffusion equation.

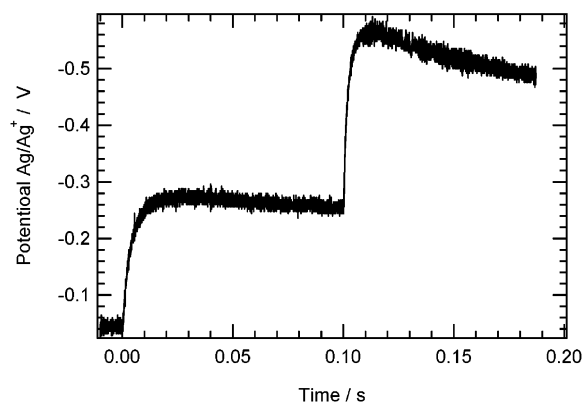


**Figure 2.** Photovoltage transit time (closed square) and maximum  $V_{oc}$  (open square), obtained from Figure 1.



**Figure 3.** Photovoltage transients from the electrodes having similar electron density ( $-400$  and  $-250$  mV vs  $\text{Ag}/\text{Ag}^+$  correspond to the electron density of  $2.5$  and  $1.0 \times 10^{17} \text{ cm}^{-3}$  in the electrodes, respectively). The transient time is proportional to the square of electrode thickness, indicating that the electron transport occurs by diffusion.

the laser intensity was controlled so that the same electron density was obtained in the electrodes. In Figure 3, the  $\tau_{TR}$  increases as the increase of electrode thickness at both different electron densities. If these transients are related with diffusion,



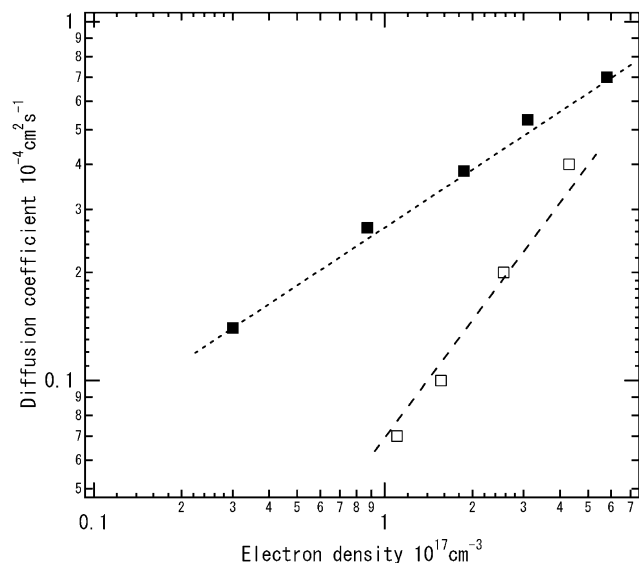
**Figure 4.** Photovoltage transients induced by two consecutive laser pulses. The pulse intensity was  $0.20 \text{ mJ}/\text{cm}^2$ .

the  $\tau_{TR}$  is proportional to the square of the electrode thickness. This relationship was seen in a plot of the square of the electrode thickness and the transit time, suggesting that the electron transport occurs by diffusion, as expected.

By using a large intensity pulse, the steady-state electron density in the electrode will be disturbed, and the state changes largely over a period of time. This makes it inaccurate to describe the electron diffusion by one effective diffusion coefficient. Thus, if  $D$  were derived from the fits to eq 3 with the transients observed here, the  $D$  shows only the average. This expects that a large deviation may be caused by different experimental conditions. To examine the influence of electron density distribution in the electrode on the transients, two consecutive pulses with the 100-ms interval were also applied to the electrodes as shown in Figure 4. In this case, electrons generated by the second pulse will transport in the electrode having a uniform electron distribution provided by the first pulse. Figure 4 shows that the  $\tau_{TR}$  of the electrons by the second pulse was shortened, and the  $\tau_{TR}$  was close to that obtained by one pulse, whose intensity was twice as high as that used here. This suggests that the initial electron density itself did not influence the transit time significantly, but the total electron density in the electrode is more likely to determine the transit time. A similar trend was seen on photocurrent transient measurements performed with and without bias light.<sup>18</sup>

**Electron Diffusion Coefficients at Open- and Short-Circuit Conditions.** To derive  $D$  from photovoltage transients, the transients were fitted with eq 3. The  $\alpha$  in eq 3 was obtained from the slope in Figure 7 shown later. Figure 1 also includes the fitted transients.  $D$  under short-circuit conditions was derived from pulse-induced current transients measured for the identical  $\text{TiO}_2$  electrodes and under the same conditions used for the photovoltage measurements.<sup>14</sup> Figure 5 shows the derived  $D$  from the  $V_{oc}$  transients in Figure 1 and  $D$  obtained from pulsed-laser-induced current transient measurements at short circuit.<sup>26</sup> The values of  $D$  at open circuit were lower than the values derived from current transients. Slower electron transport at open-circuit conditions was also reported previously by Dloczik et al.<sup>5</sup> and van de Lagemaat et al.,<sup>6</sup> who measured electron transients at open-circuit conditions by IMPS. However, uncertainty remained on the interpretation because of the influence of RC time constants on measured data.<sup>5,6</sup> Since our measurements should not be influenced by the capacitance at the interface, the fitted values of the diffusion coefficients at open circuit observed here reflect the slower electron transport in the electrodes at open circuit. Dloczik et al. also mentioned that the transient time was independent from the light intensity when the IMPS measurements were performed at open-circuit condi-



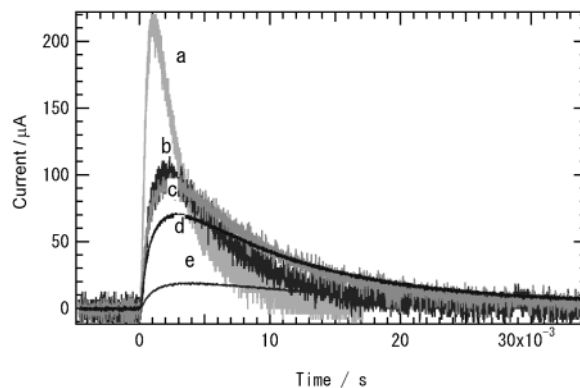


**Figure 5.** Electron diffusion coefficients at open circuit obtained by fits on the transient in Figure 1 (open square) and at short circuit obtained from current transients (closed square). The samples were prepared from nano-TiO<sub>2</sub> particles (P25) and the electrolyte was 0.7 M LiClO<sub>4</sub> in ethanol for both measurements at open and short circuit.

tions. In contrast, our results showed the light intensity dependence, which is consistent with the electron transport properties in nanoporous TiO<sub>2</sub> containing charge traps. These results show advantages and validity of the  $V_{oc}$  transient measurements.

The difference of  $D$  at the open and short circuit can also provide information how the circuit condition influences the electron transport. At both conditions, we initially neglected the electrical potential gradient in the electrodes. This assumption may not be valid for short-circuit conditions, where electrons are removed at the TCO/TiO<sub>2</sub> interface. This causes nonuniform and lower electron concentration close to the interface. This concentration gradient induces the Fermi level gradient and consequently generates the driving force toward the interface.<sup>13</sup> Under open-circuit conditions, the electron distribution becomes uniform as electrons diffuse. More uniform electron distribution for electron transport can be obtained by using bias light or consecutive laser pulses as shown in Figure 4. Under these conditions, electron transport occurs mostly by diffusion. The difference of  $D$  between open and short circuit conditions observed here suggests that the non-negligible gradient of the electrochemical potential exists not only at the TCO/TiO<sub>2</sub> interface but also through the electrode under short-circuit conditions. In this context, the deviation of measured transients in Figure 1 from fitted transients can be explained by the initial nonuniform electron distribution, that is, some degree of the electrochemical potential gradient exists just after the pulse irradiation, and the gradient will disappear as the electrons are being distributed uniformly in the electrode.

Another piece of information, which can be derived from the comparison, is about the existence of activation energy at the TCO/TiO<sub>2</sub> interface. If the energy were involved to remove electrons from TiO<sub>2</sub>, it would increase the time to collect electrons at the TCO. If this were the case, this would appear as a slower time constant in the measurement of short-circuit current transient. This is because the measured time constant is the sum of the transit times of the electrode and the interface. However, faster electron transport was observed from short-circuit than open-circuit condition. The result suggests that the time to transport across the interface does not have significant

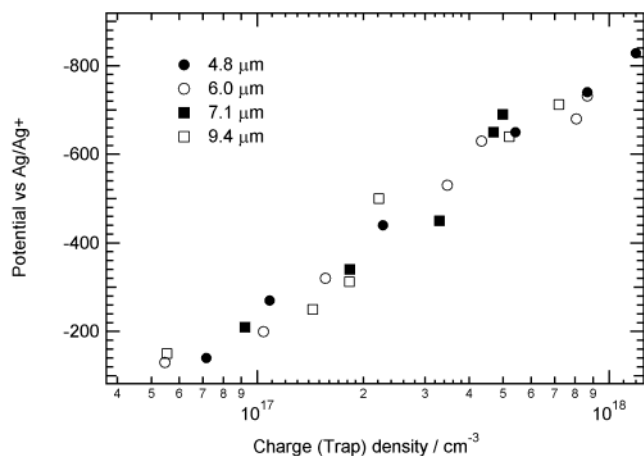


**Figure 6.** UV pulse-induced current transients from 6.6- $\mu$ m-thick TiO<sub>2</sub> electrode with additional ohmic resistors, (a) 50, (b) 490, (c) 980, (d) 1470, (e) 2450  $\Omega$ , attached to TCO. The electrode was prepared from TiO<sub>2</sub> nanoparticles (Nanoxide-T, Solaronix) and immersed in 0.7 M LiClO<sub>4</sub> in ethanol.

influence on the measured time constant, and the activation energy is less likely to exist for these TiO<sub>2</sub> electrodes on the SnO<sub>2</sub>:F substrate.

**Influence of Series Resistance on Current Transients Under Short-Circuit Conditions.** On the basis of the observations above, external resistor should also slow the electron transport. This is because the resistor increases the electron density at the TCO/TiO<sub>2</sub> interface and consequently reduces the Fermi level gradient in the TiO<sub>2</sub> electrodes. This interpretation suggests that, for short-circuit current measurements, the resistance of transparent conductive oxide layer, and a thin nonporous TiO<sub>2</sub> (under) layer, which is used to prevent electron transfer from TCO to I<sub>3</sub><sup>-</sup> in the electrolyte for DSC, should also influence the current response and complicate the analysis of  $D$  from the current responses. To examine the influence of RC components on current transients, we measured UV pulse-induced current transients with additional series resistors to TCO. Figure 6 shows the results from 6.6- $\mu$ m-thick TiO<sub>2</sub> electrodes prepared from Nanoxide-T.<sup>27</sup> As is seen, the current peak delays as increasing the series resistance. The time constant of the current decay also increases with the resistance. The integrated current showed a nearly constant value up to 1470  $\Omega$  and decreased with the increase of the resistance. The decrease may be due to too short of a time period used for integration comparing to current transient. From the peak time or the time constant of the current transient decays,  $D$  can be obtained. The  $D$  obtained from the peak time in Figure 6 was about  $10^{-5}$  cm<sup>2</sup>/s, and the value decreased with the increase of the series resistance. This seems consistent with the slower electron transport observed from open-circuit voltage transients. However, the capacitance calculated from the time constant and inserted resistance was about 10  $\mu$ F/cm<sup>2</sup> when at least more than 490  $\Omega$  was used. The order of the capacitance is consistent with the previously reported values.<sup>22</sup> This suggests that the measured current transients were influenced by both the Fermi level gradient and RC time constant, making it difficult to rule out each influence from the current transients as the circuit condition is approaching to open circuit.

**Charge-Trap Density and Distribution.** Charge-trap density in the nanoporous electrodes is an important factor affecting electron transport therein, and it has been estimated with several methods such as chronoamperometry,<sup>28,29</sup> charge extracting method,<sup>30,31</sup> light absorption measurement,<sup>32</sup> and photoelectron spectroscopy.<sup>33</sup> To estimate the charge-trap density here, two measurements, pulsed-laser-induced current transients and photovoltage transients, were employed. The number of generated



**Figure 7.** Photogenerated electron density in nanoporous TiO<sub>2</sub> electrodes and corresponding photovoltage from them. Since the electrons are captured by traps for most of the time, the electron density reflects the trap density at each potential. The trap density per energy level can be obtained by differentiating the electron density with respect to the photovoltage.

electrons by a laser pulse was obtained by integrating current transients. Electron density was obtained with measured electrode thickness and the laser spot size. Then, corresponding potential of the electron density was obtained from the photovoltage induced by the same intensity pulse used for the current measurement. Figure 7 shows a plot of the electron density and the corresponding photovoltage, measured from various electrode thicknesses. As is seen, regardless of the thickness, the photovoltage can be determined by the electron density. By assuming that all the electrons were captured by traps for most of the time, the density of charge-trap states can be obtained by differentiating the electron density with respect to the photovoltage.<sup>28,31</sup> At around  $-800$  mV and  $-200$  mV versus Ag/Ag<sup>+</sup>, we obtained the density of ca.  $3.6 \times 10^{18}$  and  $2.8 \times 10^{17}$  cm<sup>-3</sup> eV<sup>-1</sup>, respectively. These numbers were higher than previously reported results,<sup>31</sup> which were obtained from the dye-adsorbed TiO<sub>2</sub> electrodes.<sup>34</sup>

By this method, since the electric circuit was not switched from open circuit to short circuit as it was performed by the charge extraction method,<sup>30,31</sup> it would not be necessary to correct the integrated current with the charging of the TCO layer. This means that our method does not require taking into account nonfaradaic current, which potential-step chronoampelometry measurement requires. On the other hand, the experimental error comes from the pulse-to-pulse intensity variation and initial electron density variation for each measurement.

In the paper, we obtained each data plot in Figure 7 from two measurements. When the amount of photogenerated electrons by one pulse is known, the number of measurements can be reduced by using consecutive pulses to increase  $V_{oc}$  continuously as shown in Figure 4. In this case, one restriction for the experiment is that fast enough pulse repetition frequency of the laser should be used to ignore the charge recombination.

## Conclusions

To understand electron transport in TiO<sub>2</sub> nanoporous electrodes, we studied UV pulsed-laser-induced photovoltage transients. Since the electrons do not have to transport across the TCO/TiO<sub>2</sub> interface, this condition allowed us to consider the electron transport only in the electrodes. Photovoltage transients were measured with electrodes having various thicknesses, showing that the transit time was nearly proportional to the square of the electrode thickness. The transit time decreased

with the increase of the pulse intensity. These observations were in agreement with the results of the previous studies by photocurrent transient measurements at short circuit. The transients were fitted with a solution of simple diffusion equation. The fitted values of the electron diffusion coefficient were lower than that obtained from the photocurrent measurements. Although the electron transport in the nanoporous TiO<sub>2</sub> electrodes has been considered only with diffusion, the difference of the measured electron transports between open and short circuit suggested that the non-negligible gradient of the electrochemical potential existed in the electrodes under short-circuit conditions. As an experimental method, these photovoltage transient measurements can provide a tool to evaluate electron transport only in the nanoporous electrode while the short-circuit current transients may suffer from the RC time constant and possible potential barrier at TCO/electrode contact. The measured photovoltage was related with the electron density in the electrodes, showing the logarithmic increase of photovoltage with the electron density.

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- For current transients, this assumption should not be applicable to fit the current transients just after the pulse irradiation and the long tail of current decay. Otherwise, it is apparent that trap-free diffusion equation can describe the transients for some period of time, as seen in ref 18. One of the reasons why the currents transients without the assist of bias light

can be fitted with a constant  $D$  may be because that  $D$  scales with electron density ( $n$ ) with roughly  $n^{0.5}$ , which gives some tolerance to use a constant  $D$  for fitting against a few tens percent change of  $n$  during the transient.

(24) To support the validity of the neglecting recombination, we note that the amount of photogenerated electrons was proportional to the UV pulse intensity. Under the same pulse intensity, the amount decreased less than 20% as the electrode thickness increased from 4.8 to 9.4  $\mu\text{m}$ . Cyclic voltammetry was also performed with a scan rate of 100 mV/s for a conducting glass without  $\text{TiO}_2$  electrodes with 0.7 M  $\text{LiClO}_4$  in ethanol. Current increase started at around  $-630$  mV vs  $\text{Ag}/\text{Ag}^+$  and the current was a few  $\mu\text{A}$  at  $-800$  mV. In comparison to this, the maximum current of laser-induced transients measured from  $\text{TiO}_2$  electrodes by the highest pulse intensity was a few mA.

(25) Respect to the electrode thickness of the measured samples, 5–10% of electrons probably diffuse to the nonirradiated area when the electron concentration is reached to uniform distribution along the electrode thickness. We measured both short-circuit transient and open-circuit transients by a pulse having 0.09  $\text{cm}^2$  and 0.12  $\text{cm}^2$  irradiation area, and the transients were independent from the irradiation area. Thus, we assumed that electrons travel in one-dimensional space. However, this approximation is valid if the time period for analysis is short enough so that only a small portion of electrons penetrate into the nonirradiated area or if the electron diffusion length is much shorter than the radius of the laser spot.

(26) Since we obtained the same  $D$  reported in ref 14, that used the identical  $\text{TiO}_2$  electrodes and the same electrolyte, the data on the ref is used here.

(27) We did the same experiment for electrodes prepared from P25 with the series resistance and found the same tendency with Nanoxide-T. In comparison between the electrodes consisting of P25 and Nanoxide-T, both short-current transients and open-circuit transients showed that  $D$  in the electrodes consisting of P25 was lower than  $D$  in Nanoxide-T. This consistent result from the two measurements supports that this open-circuit voltage transient measurement is applicable to measure the electron transport properties in various  $\text{TiO}_2$  electrodes.

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(34) In comparison to the results found in ref 29, the electron density around  $-450$  mV vs  $\text{Ag}/\text{AgCl}$ , which is equivalent to  $-800$  mV vs  $\text{Ag}/\text{Ag}^+$ , is comparable to our results. However, the comparison in detail should be done by taking into account the difference of  $\text{TiO}_2$  preparation method, electrolytes, and surface adsorption, which are likely to influence the trap density.