

## Research Article

# Electron-Density and Electron-Lifetime Profile in Nanocrystalline-TiO<sub>2</sub> Electrode of Dye-Sensitized Solar Cells Analysed by Voltage Decay and Charge Extraction

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The dependence of the electron density and electron lifetime in nanocrystalline-TiO<sub>2</sub> electrode on the electron back reaction with I<sub>3</sub><sup>-</sup> in a dye-sensitized solar cell, based on a mesoporous titania (TiO<sub>2</sub>) matrix immersed in an iodine-based electrolyte, has been presented by analyzing the results of voltage decay and charge extraction measurements without modelling, without interpretation of mechanism, and without complicating calculations. This new analysis approach utilizes simple equations and basic definition of kinetics, concluding in absolute electron-density and charge-lifetime measurements. The relation of electron lifetime to open-circuit voltage indicates a peak of the long-lifetime charge at 5.5 V, which is consistent with the information of middle band suggested by Bisquert et al. (2004).

Mesoscopic dye-sensitized solar cells (DSCs) have been attracting intensive interest for scientific research and industrial applications because of their high photon-to-electricity conversion efficiency and low cost compared with traditional photovoltaic cells [1–4]. DSCs are constructed using a high surface area film of nanocrystalline-TiO<sub>2</sub> coated on conducting glass as working electrode. A sensitizing dye is adsorbed on the nanocrystalline-TiO<sub>2</sub>. The sandwich cell is completed by sealing a nonaqueous electrolyte containing the I<sub>3</sub><sup>-</sup>/I<sup>-</sup> couple with a second glass plate coated with a thin layer of platinum as counter electrode. The photoexcited dye injects electrons into the conduction band of the TiO<sub>2</sub> on a femtosecond to picosecond timescale [5–7], and the dye is regenerated on a microsecond timescale from its oxidised state by electron transfer from I<sup>-</sup> [8] (Figure 1). The I<sub>3</sub><sup>-</sup> formed in the reduction of dye cation diffuses to the counter electrode where electron transfer regenerates I<sup>-</sup>, which diffuses back into the porous TiO<sub>2</sub>.

At the open circuit condition, the injected electrons recombine with I<sub>3</sub><sup>-</sup>. In order to understand the mechanism

of DSC and improve the photovoltaic performance, the electron density and the electron lifetime ( $\tau_n$ ) in the TiO<sub>2</sub> conduction band at the open circuit condition have been discussed significantly.

The basic definition of  $\tau_n$  is

$$\tau_n = \frac{1}{k}, \quad (1)$$

where  $k$ , which is called time constant, is presented in an equation:

$$\frac{dN}{dt} = -kN, \quad (2)$$

where  $N$  is the number of electrons (density). There are two ways to elucidate the electron density and the electron lifetime. One way is “transient LASER spectroscopy,” which can show the density of injected electrons directly [5]. However, complete sealed cells (sandwich type) are not readily amenable for this transient LASER measurement

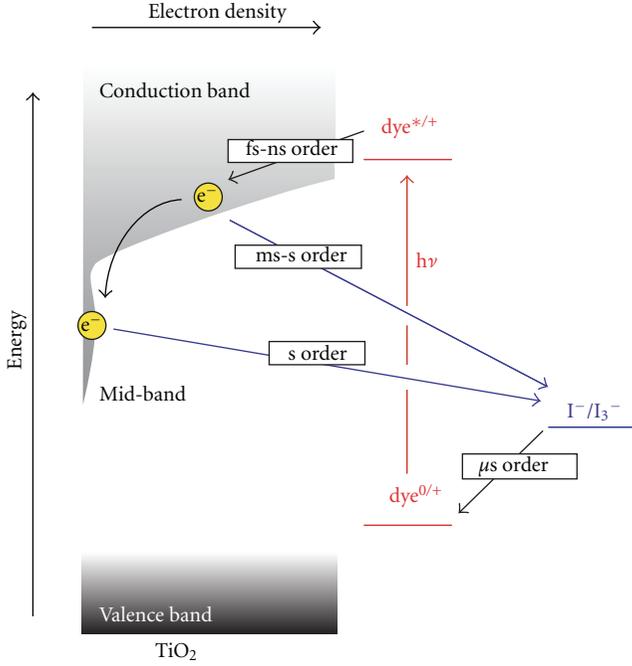


FIGURE 1: Schematic processes of photoinjected electron from  $\text{TiO}_2$  conduction band and mid-band to redox couple ( $\text{I}^-/\text{I}_3^-$ ) in DSCs on a modeled energy level diagram with electron density.

due to light scattering by the double-layered  $\text{TiO}_2$  structure [9, 10]. However, this method also requires an expensive experimental setup and demanding technique. An alternative way is to analyse the transient current and/or voltage arising from a changing light or voltage impulse. Instead of measuring the electron density directly, the amplitude methods need modelling to elucidate the electron lifetime from the results of the transient current and/or voltage between two FTO electrodes with dye-sensitised  $\text{TiO}_2$  and Pt in photovoltaic DSCs. The major amplitude methods are electrical impedance spectroscopy (EIS) [11, 12], intensity modulated photovoltage spectroscopy (IMVS) [13], and stepped light-induced transient measurement [14–17], which have elucidated the basic principles of DSCs. The electron lifetime  $\tau_n$  in the  $\text{TiO}_2$  layer is determined by the rate of the back reaction with  $\text{I}_3^-$ , and it has been found that  $\tau_n$  depends inversely on intensity (Figure 1). This means that electrons move more slowly at low light intensities, but at the same time they also react more slowly with  $\text{I}_3^-$ .

Although the amplitude methods are powerful, each method requires modelling in order to interpret the results. Therefore, due to the variety of the models and interpretations which can bias the results of  $\tau_n$ , several aspects remain puzzling. If we can obtain the absolute value of  $\tau_n$  without resorting to modelling and interpretations of the DSC mechanism, the results should be significant for DSC improvement. In order to obtain absolute  $\tau_n$ , the number of electrons (density) must be measured. For the measurement of the electron density, charge extraction method has been employed [18]. However, the relationship between the  $k$  and the electron density which has been measured by charge

extraction method has not been established. Moreover, we found the mid-band in nanocrystalline- $\text{TiO}_2$  semiconductor by analysis from voltage decay and charge extraction results. In this letter, we show an absolute  $\tau_n$  without modelling and interpretations just by connecting the  $k$  and the electron density from the charge extraction measurement, illustrated as Figure 1.

For fabrication of DSC, the detail is described elsewhere [10]. The brief procedure was shown as below. Conductive glass substrates (Nippon Sheet Glass, Solar-4 mm, 10 ohms (square) $^{-1}$  F-doped  $\text{SnO}_2$ ) were cleaned by ultrasonic bath in detergent solution, rinsed with tap water, distilled water, and ethanol, and dried. After immersion in 0.05 M  $\text{TiCl}_4$  aqueous solution at 70°C for 30 min, the porous  $\text{TiO}_2$  film was coated by screen-printing methods. In this paper, 6.6  $\mu\text{m}$  thickness of 20 nm  $\text{TiO}_2$  nanocrystalline layer was used for measurement. The  $\text{TiO}_2$  films were immersed in a  $10^{-5}$  M solution (1 : 1 mixture of acetonitrile and *tert*-butyl alcohol) of *cis*-di(thiocyanato)-*N,N'*-bis(2,2'-bipyridyl-4-carboxylic acid-4'-tetrabutylammonium carboxylate) ruthenium (II) (N719 dye) for 24 hours for dye adsorption. Cells were prepared with heat-pyrolyzed Pt coated on a second conductive glass and sealed with a hot-melt film. The electrolyte used in the cell was composed of 0.60 M butylmethylimidazolium iodide, 0.03 M  $\text{I}_2$ , 0.10 M guanidinium thiocyanate, and 0.50 M 4-*tert*-butylpyridine in the mixture of acetonitrile and valeronitrile (volume ratio: 85 : 15).

All measurements were performed in a screened dark box, and care was taken to eliminate stray light. The cells were illuminated from the substrate side with a white light emitting diode. The LED was driven by a pulse generator that synchronised the illumination pulse with the switching of the cell between open and short circuit, as previously described. When an illuminated cell has reached a steady photovoltage at open circuit, the light is then interrupted and the charge on the electrodes is allowed to decay for a given time in the dark before short circuiting the cell. The integrated current measured at short circuit corresponds to the remaining electronic charge on the conductive electrodes. The delay time between interruption of the illumination and short circuit charge extraction is varied systematically to follow the decay of electron concentration.

In order to evaluate  $k$ , (2) was transformed as follows:

$$k = -\frac{1}{N} \times \frac{dN}{dt}. \quad (3)$$

In order to relate (3) to open-circuit photovoltage ( $V_{oc}$ ), the resulting (3) was converted to the following:

$$k = -\frac{1}{N} \times \frac{dN}{dV_{oc}} \times \frac{dV_{oc}}{dt}. \quad (4)$$

Therefore, from (1) and (4), the relation for the electron lifetime to  $V_{oc}$  is

$$\tau_n = -N \times \frac{dV_{oc}}{dN} \times \frac{dt}{dV_{oc}}. \quad (5)$$

Equation (5) can be satisfied with the results of the charge extraction method and the voltage decay method by

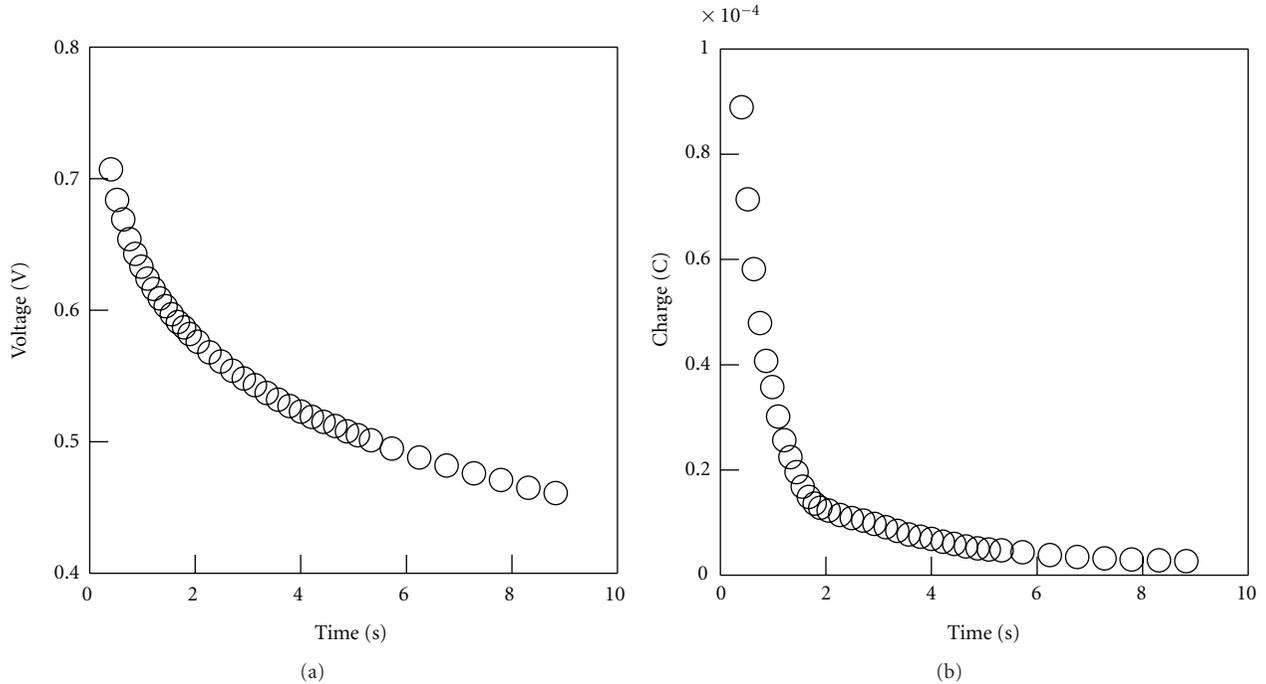


FIGURE 2: Transients of open-circuit voltage decay (a) and the extracted charge (b) after the interruption of the light on a DSC.

substituting the results by taking the average slope of each data point.

Figure 2 shows the raw results by charge extraction measurement. After the interruption of the light on the DSC, the open-circuit voltage decreased exponentially (Figure 1). On the other hand, the extracted charge (Figure 2) decreased rapidly until about 2 seconds and, then, decreased gradually afterwards. It is noticed that there is a small bump at 2.7 seconds.

Combining the results from Figures 2(a) and 2(b) gives the relationship between open-circuit voltage and the charge in the DSC (Figure 3(a)). Figure 3(b) shows the electron-density profile in  $\text{TiO}_2$  electrode related to voltage, which is derived from Figure 3(a) and  $\text{TiO}_2$  volume. There is a significant inflection point at 0.59 V, which indicates the lower edge of the conduction band (Figure 1). Consequently, the electron density is very small below 0.59 V. A small inflection at 0.54 V is perhaps indicative of mid-band in the  $\text{TiO}_2$ , as is suggested by Bisquet et al. [16].

In Figure 4(a), we present the electron-lifetime relationship between voltage and electron lifetime as derived from the results of Figures 2-3 by dividing and averaging the data points and by substituting the results in (5). There is a peak of lifetime around 0.56 V in the curve of Figure 4(a). This peak suggests the existence of a middle band in  $\text{TiO}_2$ . This fact is coincident with the analysis by the modeling by Bisquet et al. The results below the peak at 0.56 V do not follow a smooth line due to the large signal noise, because the amount of remaining charge is very small below 0.56 V (Figure 3), resulting in the very sensitive measurement. Although the lifetime is quite longer than the published results, it is significant that the peak at 0.56 V demonstrates the middle-band theory by Bisquet et al. [16]. The differences of

lifetimes are due to the elucidation methods. The lifetime of modeled result was elucidated using the number of electrons at the density of states. On the other hand, the experimental lifetime was elucidated using the total electron number in  $\text{TiO}_2$  conduction band.

Figure 4(b) shows the magnified results from Figure 4(a) around high voltage region (over 0.59 V) compared with EIS results, using an equation [12]:

$$\tau_n = C \times R, \quad (6)$$

where  $C$  and  $R$  are capacitance and resistance in a circuit, respectively.  $C$  and  $R$  are determined by fitting the EIS results of DCS under dark condition. At 0.7 V, the lifetime by electron-extraction method is significantly larger than EIS results. This difference is attributed to two points. One point is the charge lost due to recombination during the time of measurement. In the high voltage region (over 0.65 V), the recombination speed of DSC inside is very fast, resulting in the charge lost to external measurement. Therefore, under the region of slow voltage decay, this charge extraction method can work effectively. Another point is the difference in the definition of electron lifetime. The lifetime from EIS (6) is established in a field of electronics; constant  $C$  and  $R$  connected as a parallel circuit are prerequisite in order to elucidate (6) in the field of electronics engineering. In DSC, however,  $C$  and  $R$  at the interface between  $\text{TiO}_2$  electrodes and electrolyte are not stable and dependent drastically on the applied voltage. Therefore, the lifetime from EIS is so to say “a voltage-dependent time constant,” which is needed of extra interpretation in order to obtain an exact lifetime. On the other hand, the lifetime definition form (1)–(3) is straight forward and so should be free of interpretation.

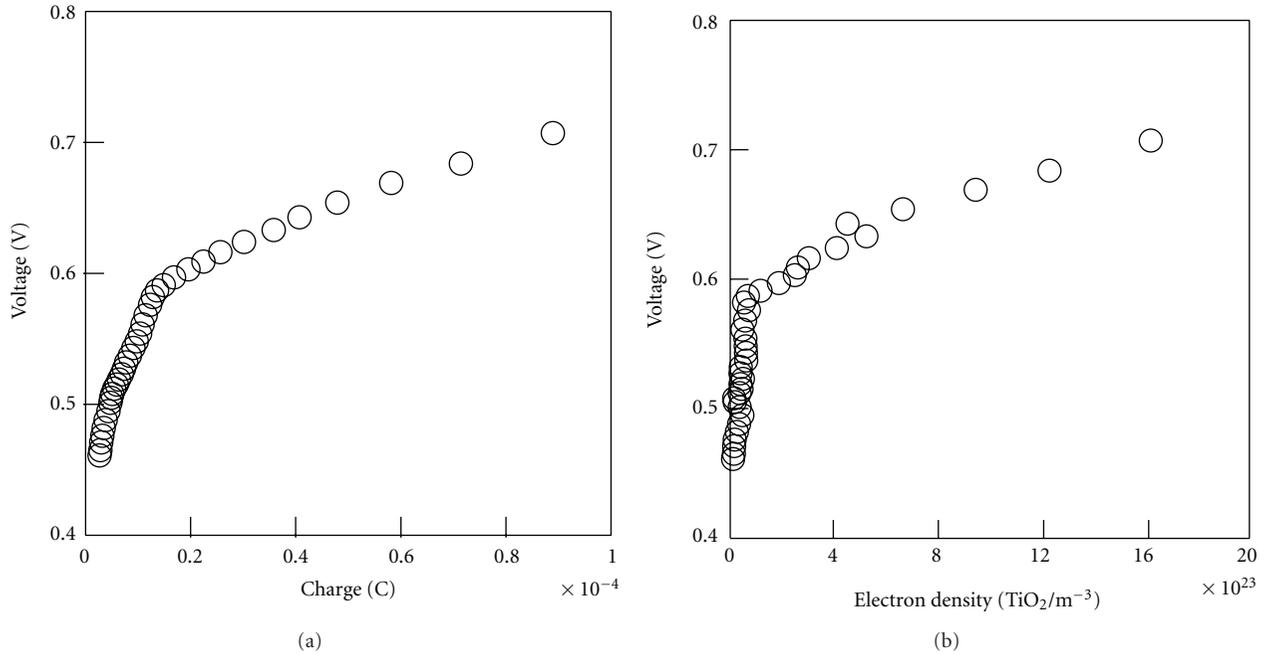


FIGURE 3: (a) Relationship between open-circuit voltage and the charge in the DSC; (b) electron density in nanocrystalline-TiO<sub>2</sub> electrode by differential of (b) and TiO<sub>2</sub> volume.

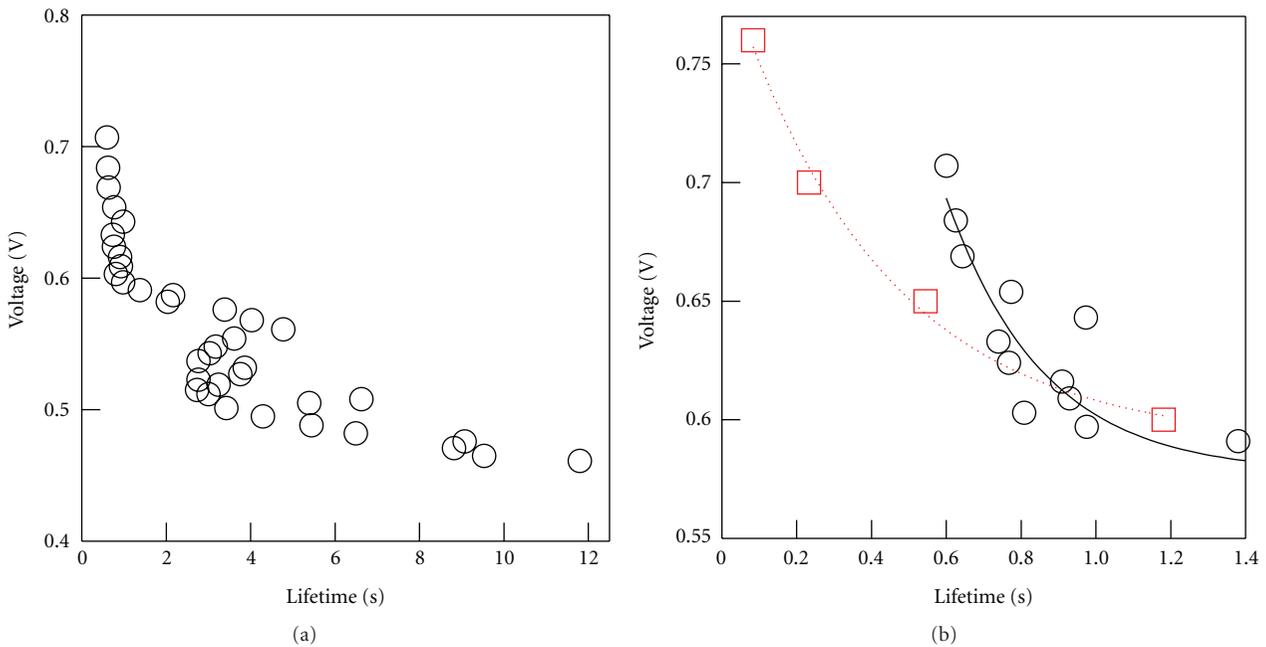


FIGURE 4: (a) The electron-lifetime relationship between voltage and electron lifetime as derived from the results of Figures 1–3 with (5); (b) magnified results in (a) around high voltage region (over 0.59 V) (○) and EIS results (□). Each line indicates an experimental fitting on the results.

We conclude that the profiles of electron density and electron lifetime in the conduction band of TiO<sub>2</sub> in DSC have been obtained using the number of charges obtained by the charge extraction method. The observed mid-band states from O'Regan et al. [15] and these measurements are coincident with the view of voltage. This  $\tau_n$  elucidation

by connecting charge extraction method and voltage decay method offers a new approach to the characterization of nanocrystalline cells. It provides direct access to the electron number as a function of voltage and decay time, so that the absolute  $\tau_n$  of the back reaction of electrons with  $\text{I}_3^-$  can be elucidated. The method allows a direct correlation to

be made between the  $\tau_n$ , photovoltage, and the number of total electrons without using modeling and interpretations, moreover without using Boltzmann factor ( $k_B$ ).

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