Quantitative Evaluation of Electron Injection Efficiency in Dye-Sensitized TiO₂ Films

Ryuzi Katoh

Abstract The efficiency of electron injection (Φ_{inj}) in dye-sensitized nanocrystalline films was studied through transient absorption (TA) and time-resolved microwave conductivity (TRMC) measurements. Here, I show the absolute value of Φ_{inj} for several dye-sensitized nanocrystalline films and discuss the relationship between Φ_{inj} and the free energy change ($-\Delta G_{inj}$) for the injection process. Some systems exhibited lower Φ_{inj} values even when $-\Delta G_{inj}$ was sufficiently large to promote electron injection. Recent experimental findings are used to propose possible explanations for this phenomenon. Quantitative evaluation of Φ_{inj} using TA and TRMC will give us new insights for developing high-performance solar cell devices.

Keywords Dye-sensitized solar cells · Transient absorption spectroscopy · Time-resolved microwave conductivity · Electron injection efficiency · Free energy change

INTRODUCTION

Since highly efficient dye-sensitized solar cells (DSSCs) were first reported (O'Regan and Grätzel 1991), much research has been carried out to improve their performance (Hagfeldt et al. 2010). As of date, solar cells consisting of Ru-complex dyes such as N719 dye, in which two protons of N3 dye¹ are replaced by tetrabutylammonium cations and black dye,² have exhibited high solar-energy-to-electricity-conversion efficiency ($\eta > 11\%$) (Chiba et al. 2006; Nazeeruddin et al. 2001). DSSCs based on metal-free organic dyes have also been extensively studied owing to these cells' potentially low production cost and the variety of molecular designs. Recently, high performance has been

achieved using porphyrin dyes (Bessho et al. 2010). However, to further improve these DSSCs, more-detailed knowledge of the mechanisms of DSSC processes, especially with regard to electron injection, is required.

Figure 1 illustrates the primary processes that occur in DSSCs. Upon photoexcitation of the sensitizer dye, the electrons are injected from the excited sensitizer dyes into the conduction band (CB) of the semiconductor film (corresponding to the “electron injection” label in the figure). The injected electrons then recombine with the oxidized sensitizer dyes, and this recombination process competes with the regeneration of the oxidized sensitizer dyes by the redox mediator molecules. The electrons can be transported in the semiconductor film as conducting electrons, which can react with redox mediator molecules or with other molecules in solution during transport before reaching the back contact electrode (“leak reaction” in the figure). Finally, the remaining electrons flow into the external circuit.

To understand the primary processes in DSSCs, the photophysical processes of dye-sensitized TiO₂ electrodes have been studied extensively by means of various experimental techniques. Electron injection is one of the most important primary processes, and transient absorption (TA) spectroscopic studies have been carried out by several research groups (Asbury et al. 2001; Kelly and Meyer 2001; Benkő et al. 2002; Durrant et al. 2006; Katoh et al. 2004; Katoh and Furube 2010). Electron injection dynamics can be studied by femtosecond TA measurements. For dye-sensitized films based on N3 and N719 complex dyes, non-exponential ultrafast electron injection

¹ (*cis*-di(thiocyanato)-bis(2,2 ϵ -bipyridyl)-4,4 ϵ -dicarboxylate)ruthenium(II); Ru(dcbpy)₂(NCS)₂.

² (BD, trithiocyanato(4,4 ϵ ,4 ϵ ϵ -tricarboxy-2,2 ϵ :6 ϵ ,2 ϵ ϵ -terpyridine) ruthenium(II); Ru(tcterpy)(NCS)₃).

Fig. 1 Primary processes in dye-sensitized solar cells

has been observed in the 100-fs to 100-ps time range (Asbury et al. 2001; Benkö et al. 2002; Katoh et al. 2004; Durrant et al. 2006). Furthermore, microsecond TA measurements are used to study the recombination of an injected electron with a parent dye-cation, and such measurements have shown that recombination occurs slowly, in the millisecond time range (Katoh et al. 2004, 2009a; Durrant et al. 2006). The signal intensities of TA measurements provide quantitative information about the efficiency of electron injection (Φ_{inj}) (Yoshihara et al. 2004a; Katoh and Furube 2010). Time-resolved microwave conductivity (TRMC) measurements can be used as an alternative technique to obtain quantitative information about Φ_{inj} (Katoh et al. 2007, 2009b). In this paper, we present our recent TA and TRMC studies on quantitative evaluation of Φ_{inj} in dye-sensitized nanocrystalline semiconductor films.

EXPERIMENTAL TECHNIQUES

Transient Absorption (TA)

Figure 2 illustrates the principles of TA spectroscopy. Sensitizer dye molecules adsorbed on the surface of a semiconductor are photoexcited by a pulsed laser. Subsequently, electron injection from the excited dye to the semiconductor occurs. Because the injected electrons and the excited and cation states of the dye have characteristic absorption bands that differ from the band observed for the dye in its ground state, these bands can be used to observe primary photochemical processes in the sample. Intermediate species also can be identified by observing TA spectra, and the decay rate of such species can be evaluated by observing the time profile of the TA signal. The

absorbance change (DA) is equal to $\log(I_0/I)$, where I_0 is the intensity of the probe light without excitation and I is that with excitation, and is proportional to the number of intermediates present in the sample.

For electron injection from an excited sensitizer dye to a semiconductor film, the absolute value of Φ_{inj} can be expressed by (Yoshihara et al. 2004a):

$$\Phi_{inj} = \frac{[N_{ox}]}{[N_{photon}]} = \frac{[N_{electron}]}{[N_{photon}]}, \quad (1)$$

where (N_{ox}) is the concentration of sensitizing dye in the oxidized state, ($N_{electron}$) is the concentration of conducting electrons, and (N_{photon}) is the number of absorbed exciting photons per unit volume. Through TA measurements (N_{ox}) and ($N_{electron}$) can be evaluated, and (N_{photon}) can be determined from the intensity of the excitation light and the absorption spectra of the samples. Thus, Φ_{inj} can be rewritten in terms of the absorbance change due to generation of the oxidized form of the sensitizer dye (ΔA_{ox}), the absorbance change resulting from generation of conducting electrons ($\Delta A_{electron}$), and the molar absorption coefficients (ϵ) of those species:

$$\Phi_{inj} = \frac{\Delta A_{ox}}{\epsilon_{ox}(1-T)N_0} = \frac{\Delta A_{electron}}{\epsilon_{electron}(1-T)N_0}, \quad (2)$$

where T and N_0 represent the transmittance of the excitation light and the number of incident excitation photons per unit area, respectively. As is evident in Eq. 2, accurate evaluation of absorption coefficient is important for reliable estimation of Φ_{inj} (Yoshihara et al. 2004a).

TA measurements of these systems have been carried out mainly by observing the bleaching of the ground-state absorption of sensitizer dyes, and the absorption due to excited and oxidized sensitizer dyes in the visible wavelength range (400–900 nm). These signals often overlap with each other, thus complicating analysis of the spectra and of decay profiles. Moreover, the assignment of the absorption bands of newly synthesized sensitizer dyes is often difficult. The observation of electrons injected into the semiconductor film is more appropriate for detailed analysis, because in the near-infrared (near-IR) wavelength range (1 000–3 000 nm), the absorption due to conducting electrons in a semiconductor film is expected to appear without overlapping other electronic absorption bands (Yoshihara et al. 2004b), such as excited and oxidized states of sensitized dyes (Fig. 2). In addition, the contribution of vibrational transition, which is expected to be observed in the longer wavelength range (>3 000 nm), is not important in near-IR wavelength range. Accordingly, observation of a wide range of wavelengths, from visible to near-IR, is essential to study primary processes in DSSCs.

After electron injection, charge recombination between a dye cation and an electron injected occurs. At higher

Fig. 2 Schematic depicting the principles of transient absorption spectroscopy and typical spectra obtained after photoexcitation of an N3-sensitized TiO₂ film

excitation intensities, the recombination occurs quickly within time-resolution of TA spectrometer, and therefore Φ_{inj} obtained is apparently suppressed. Thus, TA measurements to evaluate Φ_{inj} must be carried out under weak excitation condition. For this reason, we have developed a highly sensitive TA spectrometer (Yoshihara et al. 2004c).

Time-Resolved Microwave Conductivity (TRMC)

As described above, we have estimated the absolute value of Φ_{inj} by observing absorption due to injected electrons in the near-IR wavelength range. Many novel dyes for DSSCs have been synthesized, and the dye-cations of some of these dyes exhibit strong absorption signals in the near-IR wavelength range, thus overlapping with injected electron signals (Katoh et al. 2009c). Therefore, an alternative technique is required to evaluate Φ_{inj} quantitatively.

Recently, another method based on TRMC has been proposed to evaluate Φ_{inj} (Katoh et al. 2007, 2009b). In this method, the microwaves' electric field is used to induce oscillation of the injected electrons, and the resulting microwave absorption is observed. The intensity of microwave absorption is proportional to the number of electrons generated in the TiO₂ films. Because this method uses a microwave-cavity, the sensitivity of TRMC measurements is higher than that of conventional TA measurements. One notable drawback of TRMC is that it cannot be applied to films immersed in electrolyte solutions, because the electrolyte will strongly absorb the microwaves. Thus, a combination of TRMC and TA measurements is necessary to most accurately estimate Φ_{inj} under various conditions.

TRMC is a type of transient absorption spectroscopy that measures the conductivity (σ) of injected electrons produced by pulsed light excitation (Katoh et al. 2007, 2009b). The absorption of microwave power ($-\Delta P/P$) can be expressed as

$$\left(\frac{-\Delta P}{P}\right) = K\sigma = K'\mu[N_{\text{electron}}], \quad (3)$$

where K and K' are constants, and m is the mobility of the injected electrons. (N_{electron}) can be expressed as

$$[N_{\text{electron}}] = \Phi_{inj}I_{ex}F_A, \quad (4)$$

where I_{ex} is the intensity of excitation light and Φ_A is the fraction of absorbed light. Accordingly, Φ_{inj} can be estimated if values of K' and m are available. As an alternative method, Φ_{inj} can also be estimated by comparing experimental TRMC results with those of a reliable standard sample, such as N719/TiO₂ for which Φ_{inj} is determined through TA measurements.

RESULTS AND DISCUSSION

For electron injection processes in DSSCs, the free energy change ($-\Delta G_{inj}$) is an important parameter for characterizing the rate and efficiency of the reaction. Figure 3 schematically shows the free energy change ($-\Delta G_{inj}$) that occurs as a result of electron injection in a DSSC. The initial state of the reaction is the excited state of dye adsorbed on a TiO₂ particle, and the final state corresponds to the injection of an electron into the conduction band of the TiO₂ particle. The energy difference between these

Fig. 3 Schematic of the initial and final states of electron injection from a sensitizer dye to a TiO_2 particle in a DSSC. The energy difference between E_{LUMO} and E_{CB} produces the free energy change ($-\Delta G_{\text{inj}}$)

initial and final states corresponds to $-\Delta G_{\text{inj}}$ of the reaction. The energy of the LUMO (E_{LUMO}) of the dye is expressed as the ionization energy in the excited state, which is estimated as the sum of the oxidized potential obtained by electrochemical measurements and the high-energy edge of the luminescence spectrum. The energy of the conduction band edge (E_{CB}) of the TiO_2 films can be evaluated experimentally through electrochemical measurements. We used the value of $E_{\text{CB}} = -0.5$ V as an approximation in our studies. From the schematic, it can be seen that $-\Delta G_{\text{inj}}$ is expressed as the energy difference between E_{LUMO} and E_{CB} ($-\Delta G_{\text{inj}} = E_{\text{CB}} - E_{\text{LUMO}}$).

Figure 4 shows the molecular structures of sensitizer dyes that we have studied, and their experimentally determined Φ_{inj} values, along with $-\Delta G_{\text{inj}}$ values, are presented in Table 1. All dyes listed have positive $-\Delta G_{\text{inj}}$ values and therefore high Φ_{inj} values are expected to be observed. As is evident in Fig. 3, N719, NKX-2697, and NKX-2677 provide unity efficiency (Katoh et al. 2007). Thus, $-\Delta G_{\text{inj}}$ must be sufficiently positive to achieve a high efficiency. On the contrary, other dyes show smaller $-\Delta G_{\text{inj}}$ value. This implies that energy matching between the sensitizer dye and semiconductor film is crucial for obtaining high-performance solar cell devices. However, electron injection efficiency is not solely determined by the energy matching: other parameters can also influence Φ_{inj} in some cases. The reasons will be discussed below.

We first discuss the dye-sensitized films with the lowest $-\Delta G_{\text{inj}}$ values in Table 1, namely, BD (Katoh et al. 2009b) and NKX2311 (Furube et al. 2005). We have previously reported that for dye-sensitized ZnO films, a sufficiently high $-\Delta G_{\text{inj}}$ value (>0.2 eV) is required to obtain a high Φ_{inj} value (Katoh et al. 2002). According to that criterion, the $-\Delta G_{\text{inj}}$ values for BD/ TiO_2 and NKX2311/ TiO_2 are not sufficiently high, and therefore lower F_{inj} values are observed for these systems.

As shown in Table 1, Eosin Y has a lower Φ_{inj} value ($\Phi_{\text{inj}} = 0.2$) despite having a sufficiently high $-\Delta G_{\text{inj}}$ value ($-\Delta G_{\text{inj}} = 0.5$ eV). To understand the origin of the lower Φ_{inj} , absorption spectra of Eosin Y in the ground state were evaluated as a function of the concentration of dye adsorbed on TiO_2 . The shapes of the resulting spectra were found to be very sensitive to the concentration, thus indicating that Eosin Y aggregated on the TiO_2 surface. It has been argued that dye-aggregates exhibit fast relaxation from their excited state, so electron injection might be suppressed owing to competition with this relaxation pathway. Dye aggregation on TiO_2 has been argued frequently to explain the low performance observed for some solar cells, particularly those containing planar organic dyes.

The absorption spectra of MK-2, MKZ-40, and MKZ-41 in the ground state were not sensitive to the concentration of dye adsorbed on TiO_2 , suggesting that those dyes did not aggregate substantially. However, these dyes (Zhang et al. 2010) still exhibited low Φ_{inj} values despite having sufficiently high $-\Delta G_{\text{inj}}$ values. At present, the origin of this lower electron injection efficiency is not clear. One possible explanation is fast (ps) recombination, which is frequently observed in TA measurements (Wiberg et al. 2009; Imahori et al. 2011). After ultrafast (fs) injection of electrons, a certain number of the injected electrons undergo recombination, and the remaining electrons can be detected in our nano-second experiments. It should be noted that such long lived charge can contribute to the photocurrent.

Although several primary processes control device performance in DSSCs, electron injection efficiency is one of the most important parameters for DSSCs. TA and TRMC measurements can be used to directly and quantitatively evaluate Φ_{inj} . In particular, TRMC is widely applicable to various systems. However, this method cannot be applied to films immersed in electrolyte solutions because the

Fig. 4 Molecular structures of sensitizing dyes studied

Table 1 Electron injection efficiency (Φ_{inj}) values determined experimentally for the sensitizing dyes in Fig. 4, listed in order of decreasing free energy change for electron injection ($-\Delta G_{inj}$). Accuracy of the values is evaluated to be $\pm 10\%$

Dye	$-\Delta G_{inj}$	Φ_{inj}
MKZ-41	0.51	0.55
MKZ-40	0.5	0.7
Eosin Y	0.5	0.2
NKX-2677	0.39	1
N719	0.35	1
MK-2	0.34	0.7
NKX-2697	0.27	1
BD	0.19	0.4
NKX2311	0.17	0.5

electrolyte will strongly absorb the microwaves. Thus, a combination of TRMC and TA measurements is necessary to most accurately estimate Φ_{inj} under various conditions. We believe that these techniques provide new insights for further development of DSSCs.

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AUTHOR BIOGRAPHY

Ryuzi Katoh (✉) is a Professor at Nihon University. His research interest is physical chemistry of solar energy conversion reaction systems including dye-sensitized solar cells, photocatalysts, and organic photovoltaics.

Address: Department of Chemical Biology and Applied Chemistry, Nihon University, College of Engineering, Tamura, Koriyama, Fukushima 963-8642, Japan.

Address: National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Ibaraki, Tsukuba 305-8565, Japan.

e-mail: rkato@chem.ce.nihon-u.ac.jp