Photoinduced absorption spectroscopy of dye-sensitized nanostructured TiO₂

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Abstract

Photoinduced absorption (PIA) spectroscopy was used to investigate dye-sensitized electrodes and solar cells under illumination conditions comparable to sunlight. In the absence of redox electrolyte, *cis*-Ru(dcbpy)₂(NCS)₂-sensitized nanostructured TiO₂ films show a long-lived photoinduced charge-separation (oxidized dye molecules/injected electrons in TiO₂), with a lifetime of about 10^{−3} s under full sun illumination. The PIA spectrum of a complete dye-sensitized cell is due to electrons in TiO₂ and iodine radicals (I₂^{•−}) in the electrolyte. The lifetime of this charge-separated state at open-circuit conditions was determined to be 0.15 s (0.27 sun illumination).

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1. Introduction

Despite a large research effort some fundamental aspects of the working mechanism and kinetics of dye-sensitized solar cells are still not well understood. For instance, the recombination reaction between the injected electron and the oxidized dye molecule does not seem to follow simple first or second-order kinetics [1–4]. Another aspect is the nature of the electrons in the nanostructured metal oxide: are they free in the conduction band or mainly trapped in shallow localized states?

Laser flash photolysis studies have been used extensively to study dye-sensitized metal oxide

films. In practice, rather high laser pulse intensities are needed to obtain sufficient signal, making a direct comparison with conditions that exist under normal solar illumination very difficult.

In this Letter we will demonstrate the potential of photoinduced absorption (PIA) spectroscopy as a tool to study dye-sensitized solar cells. In PIA spectroscopy the transmission *T* through a sample is monitored, as well as small changes in transmission ΔT induced by a frequency-modulated monochromatic light beam. The ratio $\Delta T/T$ is proportional to the absorbance change ($-\Delta T/T = \ln(10) \times \Delta A$). PIA spectroscopy is frequently used in the field of conjugated polymers to investigate the nature and recombination kinetics of photogenerated species [5,6]. Recently, PIA measurements at a single wavelength in the near-infrared (frequency-resolved modulated

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transmission) have been used to study dye-sensitized solar cells [7,8]. In this Letter we will present PIA spectra for both dye-sensitized solar cells and dye-sensitized TiO₂ films kept in air and determine the recombination rates under varying conditions from the frequency dependence of the PIA signals.

2. Experimental

Transparent nanostructured TiO₂ films (thickness 5 μ m, particle size 12–15 nm) were prepared as described earlier [9]. The films were stained in a dye bath containing 0.5 mM *cis*-Ru(dcbpy)₂(NCS)₂ (Solaronix, Switzerland) in ethanol and left overnight. Complete dye-sensitized solar cells were assembled using a thermally platinized tin oxide glass counter electrode and a Surlyn frame as a spacer and sealant. The electrolyte was 0.5 M LiI, 0.05 M I₂ and 0.5 M 1-methylbenzimidazole in 3-methoxypropionitrile. 1-Methylbenzimidazole is added to improve the photovoltage of the solar cell (similar to 4-*tert*-butylpyridine).

2.1. Photoinduced absorption set-up

Light from a green He–Ne laser (Coherent, 543.5 nm) was mechanically chopped and used to excite the sample. The beam was expanded to about 1 cm² and had an intensity of about 2.4 mW cm⁻². White probe light was provided by a tungsten–halogen lamp equipped with a 5 cm water filter. The probe light was attenuated using neutral density filters and had an intensity corresponding to 0.0027–0.27 sun (1 sun = 100 mW cm⁻² with AM1.5 G spectral distribution). The intensity was measured using a color-compensated Si photodiode (type BPW21R) that has a spectral response similar to the dye-sensitized TiO₂. The transmitted probe light was focused onto a monochromator (Acton Research Corporation SP-150) and detected using a UV-enhanced Si photodiode (CVI model AD221), connected to a current amplifier (Keithley model 427) and lock-in amplifier (Stanford Research Systems model SR830). PIA measurements were done at room temperature.

3. Results and discussion

3.1. Ru(dcbpy)₂(NCS)₂-sensitized TiO₂

Fig. 1a shows the photoinduced absorption spectrum of a nanostructured TiO₂ film sensitized with *cis*-Ru(dcbpy)₂(NCS)₂ (also known as N3-dye) in the absence of electrolyte. A positive $\Delta T/T$ signal, corresponding to a bleach, is found in the 400–600 nm region and a negative signal at wavelengths longer than 600 nm. As expected, the spectral characteristics are similar to those found in nanosecond laser flash photolysis of the N3–TiO₂ system [1,3,4,10] and in radiolysis of N3 in solution [11]. They correspond to the differential spectrum of oxidized N3 dye, with a bleach of the ground state MLCT absorption and an absorption feature around 760 nm that can be ascribed to NCS $\rightarrow$ Ru^{III} LMCT transitions [1]. A small contribution due to absorption by electrons in the TiO₂ will also be present in the PIA spectrum. Contributions of excited state absorption and luminescence of the dye are negligible.

The PIA-signal is phase shifted with respect to the modulated excitation, except at very low modulation frequencies. The frequency dependence of the magnitude and the phase shift of the $\Delta T/T$ signals give information on the recombination kinetics between the injected electrons in the TiO₂ and the oxidized dye. In Fig. 1b the amplitude of the $\Delta T/T$ signal is plotted as function of the chopping frequency. As the frequency decreases, the signal approaches a maximum level, which corresponds to the absorption of the steady-state concentration of oxidized dye and electrons in the TiO₂ resulting from continuous laser excitation. The intensity of the white probe light has a strong effect on the magnitude and the frequency response of the $\Delta T/T$ signal. This is due to significant excitation of the sample by the probe beam. Increasing the white probe light intensity leads to smaller $\Delta T/T$ signals and more rapid recombination kinetics as will be shown later. At higher frequencies, the $\log(\Delta T/T)$ – $\log(\text{frequency})$ plot approaches a slope of -1 . This is expected for monomolecular and bimolecular decay processes [6]. For stretched exponential decay, however, a slope between 0 and -1 is expected.

Fig. 1. (a) Photoinduced absorption spectrum of a *cis*-Ru(dcbpy)₂(NCS)₂-sensitized nanostructured TiO₂ film in air. Chopper frequency 17 Hz, white probe light intensity 0.083 sun. (b) Frequency dependency of the $\Delta T/T$ signal recorded at 800 nm. The white probe light intensity was varied between 1% and 100% as indicated (100% = 0.27 sun). The dotted line has a slope of -1 . (c) Complex plane plots of the photomodulated transmittance (800 nm). Inset: recombination rate as function of bias light intensity.

In Fig. 1c results of frequency-dependent PIA measurements are shown in complex plane plots, where the 90° out-of-phase (imaginary) $\Delta T/T$ signal is plotted against the in-phase (real) component. Slightly flattened semi-circles are observed. The time constant for the recombination reaction ($\text{N3}^+ + \text{e}^-(\text{TiO}_2) \rightarrow \text{N3}$) was determined by using a fitting program for impedance spectroscopy, Equivalent Circuit [12]. The semi-circles were fitted using a parallel RQ -circuit, where Q is a non-ideal capacitor (constant phase element) with an impedance $Z = (Q(i\omega)^n)^{-1}$, where ω is the angular frequency. The exponent n (≤ 1) is a measure for dispersion of the time constant. In the case of ideal first-order recombination, n is expected to be one. Time constants are determined using $\tau_r = (RQ)^{1/n}$. The fit results are shown in Table 1.

There is a linear relation between the recombination rate constant ($k_r = 1/\tau_r$) and the probe light intensity, see the inset in Fig. 1c. This can be explained, assuming first-order kinetics, as follows: Species A, that is generated by the laser light, has a decay rate $s = k_r[\text{A}]_{\text{laser}}$. Additional bias light gives rise to a constant concentration of A, $[\text{A}]_{\text{bias}}$, and the decay rate becomes: $s = k([\text{A}]_{\text{laser}} + [\text{A}]_{\text{bias}})$. In the PIA method, the constant offset caused by the bias light is not observed in the frequency-modulated ΔT or in the steady-state transmission T (the change in T due to the bias light is very small). The PIA data is analysed as a pseudo first-order reaction: $s = k'_r[\text{A}]_{\text{laser}}$. The observed first-order rate constant k'_r is related to the true first-order rate constant k_r as follows: $k'_r = k_r([\text{A}]_{\text{laser}} + [\text{A}]_{\text{bias}})/[\text{A}]_{\text{laser}}$. As $[\text{A}]_{\text{bias}}$ varies linearly with bias light, also k'_r will vary linearly with bias light. The true k_r

Table 1

Time constants for the back reaction of electrons in TiO₂ with oxidized N3 dye (no electrolyte present)

Probe light intensity (%)	$\tau_r/10^{-3}$ s	$\Delta T/T_{\text{ss}}$	n
100	3.0	7.8×10^{-5}	0.83
30	6.8	1.9×10^{-4}	0.87
10	12.6	3.6×10^{-4}	0.89
1	20.3	5.8×10^{-4}	0.91

Fit results of the PIA-data shown in Fig. 1c. The fitting procedure is described in the text. $\Delta T/T_{\text{ss}}$ is the $\Delta T/T$ in 'steady state', i.e., in the low-frequency limit.

is found at zero bias light intensity. It should be noted that the observed linearity of is no proof for a first-order recombination mechanism. Following a similar approach it can be shown that linear dependence will also be found in a second-order reaction when $[A]_{\text{bias}} \gg [A]_{\text{laser}}$.

The PIA investigation of $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$ -sensitized TiO_2 suggests that under full sunlight the lifetime of the charge-separated state is about 1 ms. This value is much longer than previously suggested by some investigations using laser flash photolysis [3,4]. On the other hand, Haque et al. [13] found time for half-decay of 3 μs to 1 ms depending on the laser pulse intensity of 6–0.04 mJ cm^{-2} , respectively. Analysis of their data was done assuming a stretched exponential decay [14]. The marked differences between our present study and those by Durrant and co-workers can probably be attributed to the application of a constant white bias light in our experiments, that gives rise to a constant bias level of electrons in the TiO_2 . As this is also the case in real dye-sensitized solar cells, PIA measurements provide a convenient way of measuring the recombination rate of electrons with oxidized dye molecules.

3.2. Complete dye-sensitized solar cell

In Fig. 2a, PIA spectra of a complete dye-sensitized solar cell are shown. The absorption increases with wavelength up to 800 nm and remains flat up to 1200 nm. The shape of the spectra is similar under open and short-circuit conditions, but the magnitude of the signal is higher under open-circuit conditions. We attribute the PIA signal to electrons in nanostructured TiO_2 and iodine radicals (I_2^-). Upon illumination, dye molecules are excited and can inject electrons into the TiO_2 . The remaining oxidized dye is reduced very rapidly by the iodide that is present in a high concentration in the electrolyte. This reaction leads to the formation of I_2^- radicals that disproportionate to form triiodide and iodide.

Electrons in nanostructured TiO_2 exhibit a very broad absorption and have an extinction coefficient of about $1000 \text{ M}^{-1} \text{ cm}^{-1}$ at 800 nm [15]. Triiodide does not absorb at wavelengths larger than 600 nm, while I_2^- exhibits a broad absorption

Fig. 2. (a) Photoinduced absorption spectra of a complete *cis*- $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$ -sensitized nanostructured TiO_2 solar cell under open-circuit (OC, filled symbols) and short-circuit conditions (SC, open symbols). The chopping frequency was 17 Hz, white probe light intensity 0.027 sun. (b) Complex plane plots of the photomodulated transmittance at 800 nm. The bias light intensity was 10% or 100% (0.27 sun) as indicated.

peak around 750 nm with an extinction coefficient of $2200 \text{ M}^{-1} \text{ cm}^{-1}$ [16]. Recently, it was shown in pulsed nanosecond laser studies that I_2^- is an important long-lived intermediate in the dye-sensitized solar cell [17–19]. The PIA spectra in Fig. 2a have contributions of both electrons and I_2^- radicals. Under short-circuit number of electrons accumulated in the nanostructured TiO_2 will be less

Table 2

Parameters extracted from the PIA experiments shown in Fig. 2b

Probe light intensity (%), OC/SC conditions	$\tau_r/10^{-3}$ s	$\Delta T/T_{ss}$	n	$e^-/\text{particle}$
100, OC	51.4	1.5×10^{-4}	0.94	0.90
100, SC	8.3	2.2×10^{-5}	0.80	0.13
10, OC	151	4.3×10^{-4}	0.90	2.6
10, SC	31.5	7.9×10^{-5}	0.79	0.47

OC = open-circuit, SC = short-circuit. The number of electrons per TiO_2 nanoparticle was calculated from $\Delta T/T_{ss}$ using an extinction coefficient of $1000 \text{ M}^{-1}\text{cm}^{-1}$ and an estimated 2×10^{14} TiO_2 particles cm^{-2} ($\Delta T/T_{ss}$ was multiplied by 2 to convert the RMS value of ΔT measured by the lock-in amplifier into a peak–peak value).

than under open-circuit conditions, which explains the difference in the observed PIA spectra.

The results of frequency-dependent PIA measurements are shown in the complex plane in Fig. 2b. Slightly depressed semi-circles are found. The extracted parameters are listed in Table 2. The following observations can be made: (I) Change from open-circuit to short-circuit conditions leads to a decrease in $\Delta T/T$ amplitude and a smaller time constant. (II) Increase in bias light intensity leads to a decrease in $\Delta T/T$ amplitude and a smaller time constant. It is clear that there will be less accumulation of electrons in the nanostructured TiO_2 under short-circuit conditions, as the electrons are continuously extracted as a current. This leads to a smaller $\Delta T/T$ under short-circuit conditions and a shorter time constant. In open-circuit, the only decay mechanism for the accumulated electrons in the nanostructured TiO_2 is the reaction with redox species in the solution (I_3^- and I_2^-). In this case, the observed time constant corresponds to the lifetime of the electron, but there can also be a contribution due to I_2^- . The time constant decreases with increasing bias light, as was observed earlier using intensity-modulated photovoltage measurements (IMVS) [20,21]. The 3-fold decrease in time constant is in good agreement with [21], where the lifetime was found to vary with the inverse square root of the light intensity. In an additional experiment the modulated photovoltage was measured as function of the chopping frequency under open-circuit conditions. There is a clear correlation between the photo-modulated voltage and transmission signal: their ratio was constant at all frequencies, which suggests that the contribution of I_2^- to the PIA signal

is relatively small. As the electron absorption dominates at low modulation frequencies, the electron concentration in the nanostructured TiO_2 can be calculated, see Table 2. Depending on bias light and open/closed-circuit conditions, 0.1–3 electrons per TiO_2 particle are generated by continuous laser excitation (2.4 mW cm^{-2}).

Some marked differences are found when comparing our PIA results with those of Franco et al. [7] and Zhu et al. [8]. In these studies no significant difference in time constant was found when changing from short-circuit to open-circuit, whereas a fivefold increase is found in this study. Franco's explanation was that mainly trapped electrons were monitored at the detection wavelength of 940 nm [7]. In Zhu's study, the frequency dependence of their PIA signals at open-circuit was attributed to recombination processes at the substrate.

To summarize, photoinduced absorption spectroscopy can be a valuable tool in the study of dye-sensitized solar cells. We have demonstrated that spectral and kinetic information can be obtained using low excitation intensities (<1 sun) with complete cells or separate photoelectrodes. In a forthcoming paper we will report on PIA-measurements in an extended spectral range (350–2000 nm) and on the combination of PIA with modulated photovoltage and photocurrent techniques.

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