

Trapping of electrons in nanostructured TiO₂ studied by photocurrent transients

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Abstract

The electron transport in nanostructured TiO₂ has been investigated in an electrochemical system using laser flash induced photocurrent transient measurements with additional continuous monochromatic bias light. Significant effects are found on the photocurrent transient depending on the wavelength of the bias light (360–480 nm). The electron transport time is shorter and the total collected charge is higher when the bias light is in the UV region, while increased transport times and a decreased charge is found with visible light bias. These effects can be explained by trap filling by the UV bias light in the first case and by emptying of traps by visible bias light in the latter.

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1. Introduction

Dye-sensitized nanostructured solar cells (DNSCs) are a new class of potentially low cost solar cells. In these photoelectrochemical cells, a nanostructured metal oxide film with dye molecules chemisorbed at its surface forms the photoactive material. TiO₂ in the anatase crystalline form is the most studied material for nanostructured electrodes. An interesting feature of the DNSC is that the transport of electrons in the nanostructured film is relatively slow. Time- and frequency-resolved photocurrent measurements show that time needed to collect photoinjected electrons at the back contact depends strongly on the light intensity, ranging from less than a millisecond at high light intensities to more than a second in near-dark situations [1–5].

Because of their small size and low doping density, the individual particles from which a nanostructured metal oxide electrode is built up do not contain a significant electric field inside. As the nanoparticles are surrounded by electrolyte, no significant macroscopic electric field exists in the nanostructured film. Electron transport is therefore thought to occur by diffusion [5–7]. Experimental data is to a large extent in agreement with diffusive transport of electrons. The diffusion coefficients that are calculated are, however, strongly dependent on the light intensity and electron concentration in the nanostructured film [1–5,8] and also

on the concentration of ions in the electrolyte [7,9]. The latter effect can be explained by the fact that electrons in the nanostructured films are charge-compensated by ions in the solution. The diffusion coefficient that is measured is a so-called ambipolar diffusion coefficient, that depends on both concentration and diffusion coefficient of the electrons in the nanostructured film and the ions in the electrolyte [5,9]. In practical DNSCs, the ion concentration in the electrolyte (0.5 M cations + 0.5 M anions = $6 \times 10^{20} \text{ cm}^{-3}$) exceeds the electron concentration (1 electron per particle, $10^{17} \text{ particles cm}^{-3}$) by orders of magnitude, so that the measured diffusion coefficient is essentially that of the electrons. The measured diffusion coefficient in nanostructured TiO₂ is much lower than that in TiO₂ (anatase) single crystals and thin dense films. Furthermore, it is a function of the electron concentration in the nanostructured film. Both observations can be explained by trapping of electrons [1–3,5]. If part of the electrons is trapped, the apparent diffusion coefficient decreases as only the free conduction band electrons diffuse. The change in apparent diffusion coefficient with total electron concentration can be explained by a change in the ratio of free to trapped electrons, which occurs if the quasi-Fermi level changes with respect to the conduction band.

Little is known about the nature of traps in nanostructured metal oxide films. Because of the high surface-to-volume ratio of the nanostructured film, it is quite likely that traps are located at the semiconductor–electrolyte interface. Alternatively, traps may be located at the many grain boundaries between the individual nanoparticles. An exponential

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distribution of trap state energies is frequently proposed in order to fit the electron transport data [8–10]. Most of these traps are located within 0.1 eV of the conduction band edge. Van de Lagemaat and Frank [11] modeled the electron transport in a dye-sensitized nanostructured TiO₂ film using a random walk approach. They estimated that the density of trap states is in the order of 1 per particle.

A relatively deep trap state in nanostructured TiO₂, about 0.5 eV below the conduction band, has been observed by transient photocurrent measurements [12], spectroelectrochemistry [13] and chronoamperometry [14]. The energetic level of the traps shifted with 72 meV per pH unit and the density of the traps ranged from about 1 per nanoparticle at pH 4.7 to about 100 at pH 13 [14]. These observations clearly suggest that this trap is a surface state.

In this paper, we investigate the effect of a continuous monochromatic bias light on laser pulse-induced photocurrents in nanostructured TiO₂. The idea behind this is that bias light, even at low intensities, may affect trap states in the TiO₂ and can give a change in the transport of electrons through the nanostructured film. Indeed, significant effects are found on the electron transport time and on the total collected charge in the photocurrent transient when using bias light with a wavelength of 360–480 nm. The results are explained in terms of filling and emptying of traps by the bias light prior to the laser pulse.

2. Experimental

2.1. Preparation of TiO₂ electrodes

Nanostructured TiO₂ electrodes were prepared by a compression method [15]. A TiO₂ suspension was prepared by adding Degussa P25 TiO₂ powder (20 wt.%) to spectrograde ethanol and stirring overnight. The suspension was applied onto a conducting glass substrate (TEC8, Libby–Owens–Ford) by doctor blading using scotch tape as frame and spacer. After drying, the tape was removed and a 50 μm thick aluminum foil was placed on the film. The package was then put in between two planar steel plates and pressure of 1500 kg cm⁻² was applied. Finally, the nanostructured electrodes were sintered at 450 °C in air for 5 min to improve their mechanical stability.

2.2. Laser-induced photocurrent transients

The electron transport in nanostructured TiO₂ films was studied using time resolved photocurrent measurements [7]. The setup consists of an electrochemical system, a pulsed laser and a continuous monochromatic light source, see Fig. 1. A quartz cuvette serves as the electrochemical cell, with a nanostructured TiO₂ electrode as working electrode (area 1 cm²), an Ag/AgCl reference electrode and a large area platinum counter electrode. The potential is controlled with fast potentiostat (EG&G 273), which is connected to a

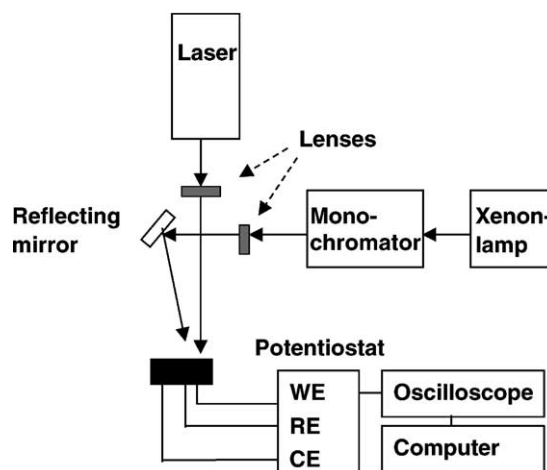


Fig. 1. Experimental setup for laser-induced photocurrent transient measurements modified with monochromatic bias light.

digital oscilloscope (Hewlett-Packard 54600A) in order to monitor the current transients. A single-shot excimer laser (ELI-94 Estonian Academy of Sciences) provides light pulses with a duration of 30 ns at a wavelength of 308 nm. The intensity of the laser is measured before and after experiments using a joulemeter and shows reasonable equal values that assures good reproducibility. The intensities used in this study were between 0.10 and 0.35 mJ. Monochromatic bias light is provided from a 450 W xenon lamp, fitted with a 60 mm water filter, in combination with a 1/4 m monochromator. The intensity from the bias light was held at constant at $\sim 10 \mu\text{W}$. Each photocurrent transient is an average of at least eight recordings with intervals long enough to assure good reproducibility, allowing the transient to decline completely (approximately 60 s). The nanostructured TiO₂ electrode is illuminated from the electrolyte/electrode interface side. The electrode is illuminated homogeneously by defocusing the laser beam, with approximately 20% of the laser pulse hitting the electrodes. If not otherwise stated the electrolyte used was 0.7 M LiClO₄ in ethanol (air saturated) and the applied potential +300 mV vs. Ag/AgCl in ethanol.

3. Results

Typical laser pulse-induced photocurrent transients are shown in Fig. 2a. The UV laser pulse is absorbed in the outermost few hundred nanometers of the nanostructured TiO₂ film [7], resulting in the creation of electron–hole pairs. A large part of the electrons and holes recombines directly. At the lowest laser intensity the recombination is about 50%, but this fraction increases strongly with pulse intensity. The holes that do not recombine with electrons react with the electrolyte, as ethanol is an effective hole scavenger for TiO₂. The remaining electrons can travel through the nanostructured TiO₂ film to the conducting substrate, where they are collected and registered as a current.

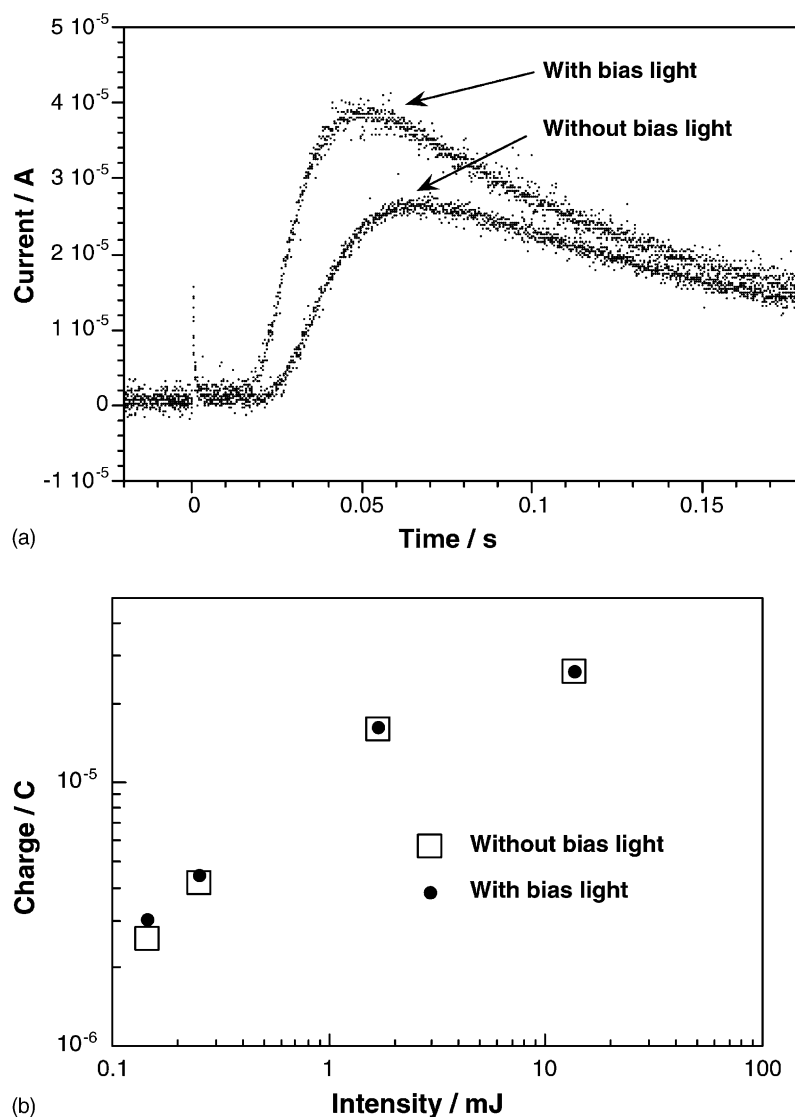
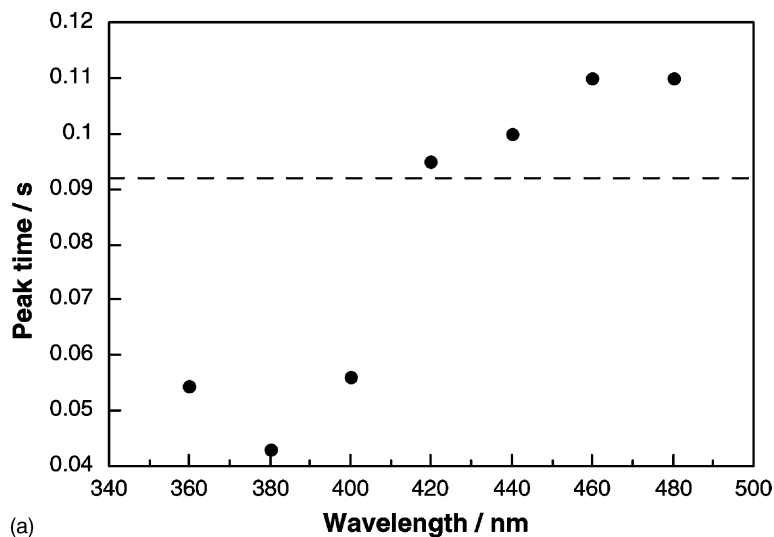


Fig. 2. (a) Photocurrent transients of a nanostructured TiO_2 film (thickness $10 \mu\text{m}$) with and without bias light (400 nm). (b) Total amount of charge vs. laser pulse intensity, with and without bias light, plotted on a logarithmic scale. The electrolyte was 0.7 M LiClO_4 in ethanol and the potential was $+300 \text{ mV vs. Ag/AgCl}$.

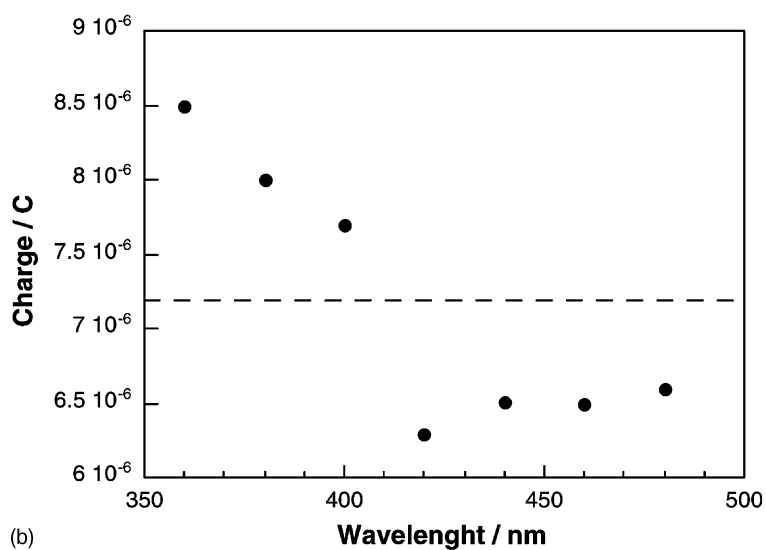
Application of a continuous monochromatic bias light with a wavelength of 400 nm has a significant effect on the photocurrent transient, see Fig. 2a. The time at which the maximum current is recorded (t_{peak}) is shortened and the total collect charge, obtained by integrating the photocurrent transient, has increased. These effects can only be observed if the laser pulse intensity is relatively low, see Fig. 2b. The effect of the wavelength of the bias light on the photocurrent transients was investigated and the results are shown in Fig. 3. Bias light with a wavelength of $\leq 400 \text{ nm}$ gives a decrease in t_{peak} , while wavelengths of 420 nm and higher gives an increase (Fig. 3a). At the same time the total charge collected increases with bias light $\leq 400 \text{ nm}$ and decreases with bias light $\geq 400 \text{ nm}$. The experiment was repeated several times with different TiO_2 electrodes and same trend was always found. The same trend was also found when the

electrolyte was deoxygenated by purging with N_2 , see Fig. 4. A few laser shots were fired before the actual measurement to ensure removal of any oxygen adsorbed at the TiO_2 surface. The collected charge was slightly increased compared to the experiment in air, because the losses of electrons to oxygen in the electrolyte are lower.

The effect of composition and concentration of the electrolyte on the photocurrent transients of nanostructured TiO_2 was also investigated. The same general effect the monochromatic bias light was found when tetrabutylammonium perchlorate (TBA-ClO_4) was used instead of lithium perchlorate (LiClO_4), although the transient was somewhat slower and less charge was collected. In the electrolyte series 0.7, 0.07 and 0.007 M LiClO_4 in ethanol the current transient also slowed down and a reduction of the collected charge was observed. The general effect of monochromatic



(a)



(b)

Fig. 3. (a) Peak current time of the photocurrent transient vs. wavelength of the bias light. (b) Total amount of charge collected vs. wavelength of the bias light. The dotted line parallel to the x -axis corresponds to the values obtained without bias light. Conditions as in Fig. 2.

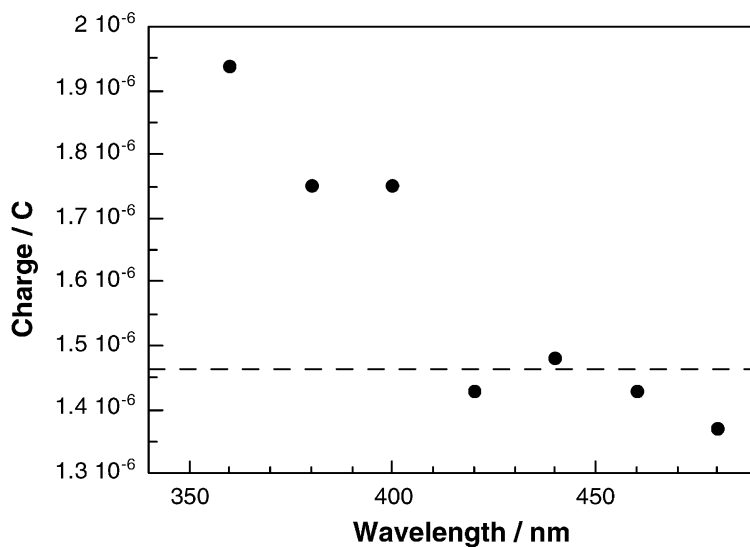


Fig. 4. The collected charge of the photocurrent transient vs. wavelength of the bias light in a rigorously deaerated system. The dotted line corresponds to the value obtained without bias light. Conditions as in Fig. 2, except that the electrolyte was purged with N_2 .

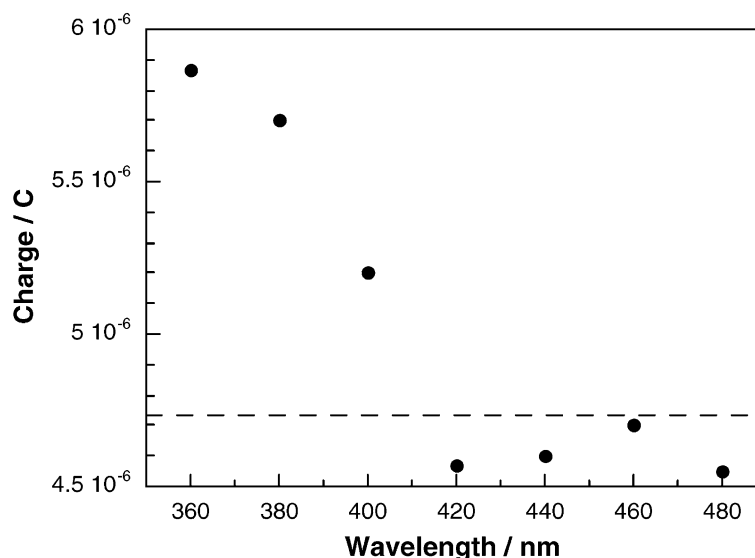


Fig. 5. Charge of the photocurrent transient vs. wavelength of the bias light in aqueous electrolyte. The electrolyte was an aqueous solution of 0.1 M KI, pH 6.6, and the applied potential +300 mV vs. Ag/AgCl. The dotted line is the total charge collected without bias light.

bias light was unchanged. The same was found when the electrolyte was changed to 0.1 M KI in water (pH 6.8), see Fig. 5.

4. Discussion

The general characteristics of the laser-induced photocurrent transient of the compressed nanostructured TiO₂ electrodes are similar to those recorded with transparent sol-gel type nanostructured TiO₂ electrodes published previously [7]. The shape of the photocurrent transients can be well-described by assuming that the electrons travel through the nanostructured film by diffusion. An apparent diffusion coefficient (D) can be calculated from the film thickness (W) and t_{peak} using Eq. (1) [7]:

$$D = \frac{W^2}{6t_{\text{peak}}} \quad (1)$$

Values of D in the order of $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ are typically found in this study. The electrons in the nanostructured TiO₂ film are charge compensated by ions in the electrolyte solution. The movement of electrons is therefore affected by the electrolyte. When the concentration of the electrolyte is lowered, electron transport in the nanostructured TiO₂ slows down. If the concentration of ions in the electrolyte is much higher than that of the electrons in the TiO₂, the measured diffusion coefficient is equal to the apparent diffusion coefficient of electrons in nanostructured TiO₂.

The value of D in the order of $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ is orders of magnitude smaller than the diffusion coefficients derived from mobility measurements of anatase dense films [16] and single crystals [17] ($0.1\text{--}0.5 \text{ cm}^2 \text{ s}^{-1}$). This large difference can be due to trapping of electrons in the nanostructured

film [1–3,5]. Only the fraction of electrons that is free in the conduction band contributes to the diffusion. By applying monochromatic bias light in the photocurrent transient measurement information on the traps can be obtained.

The compressed films are made from Degussa P25 TiO₂ powder, which contains approximately 75% anatase and 25% rutile nanocrystals with a size of about 25 nm. The bandgaps of anatase and rutile are 3.2 and 3.0 eV, respectively. Bias light with a wavelength shorter than 410 nm results in the generation of electron-hole pairs in the nanostructured TiO₂ film. While the holes are scavenged by the electrolyte, the electrons can move through the film and will have two functions: first they will fill up part of the available traps and second, they can react with electron acceptors in the electrolyte. Electrons from the laser pulse will encounter less empty traps and reach the conducting substrate more rapidly. Furthermore, these electrons will encounter less acceptors in the electrolyte, resulting in an increased collected charge from the laser pulse. The shorter peak current time and the increase in collected charge in the presence of UV bias light can therefore be easily explained. The apparent diffusion coefficient increases from $1.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (without bias light) to $1.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (360 nm bias light).

The effect of the bias light with a wavelength of 420–480 nm can be explained by assuming that additional traps are created by this light. This would result in a slower photocurrent response and a decreased collected charge. The most likely mechanism is that initially filled traps are emptied by excitation with visible light. A small photocurrent (less than 1 μA) is in fact detected upon visible bias light illumination, in accordance with this assumption. Boschloo and Fitzmaurice [13] found in a spectroelectrochemical study that electrons trapped in surface states of a nanostructured TiO₂ electrode exhibit an optical absorption in

the 400–550 nm region. This wavelength range corresponds roughly to the region where the visible monochromatic bias light has a significant effect on the photocurrent transients in this study. The energy position of the surface states was about 0.5 eV below the conduction band edge of TiO₂ [13]. They can be regarded as deep traps, as there is not a significant thermal escape of electrons possible from these traps on the timescale of the photocurrent transients. The effect of the visible bias light on the transport speed of the electrons in the nanostructured TiO₂ electrode is therefore most likely due to a decrease in the number of electrons in the conduction band due to increased deep trapping.

The nature of the deep trapping sites at the TiO₂ surface can be oxygen vacancies. One missing surface oxygen atom will result in two adjacent Ti³⁺ sites. O₂ adsorbs strongly at these sites [18], presumably under the formation of Ti⁴⁺–O₂²⁻ species. We propose here that this species is the deep trap observed in nanostructured TiO₂. When an electron is trapped, a titanium peroxide (Ti⁴⁺–O₂²⁻) species can be formed which is known to exhibit a yellow color. This is in agreement with the observation of a weak absorption at about 400–550 nm for filled surface states in nanostructured TiO₂ [13]. It is noted that these surface states are deep traps that are probably of a lesser importance in the trapping–detrapping process that has been proposed to explain the small diffusion coefficients found in dye-sensitized nanostructured TiO₂ solar cells.

5. Summary

We demonstrated the effect of a low-intensity continuous monochromatic bias light on the laser-induced photocurrent transients of nanostructured TiO₂. A faster electron transport and an increased collected charge are found by using UV bias light and a slower transport and a decreased collection of electrons with visible bias light. These results can be explained by the effect that the bias light has on the population of (deep) traps in the nanostructured TiO₂ film.

Acknowledgements

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