

Influence of a TiCl₄ Post-Treatment on Nanocrystalline TiO₂ Films in Dye-Sensitized Solar Cells

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In this study, the influence of the TiCl₄ post-treatment on nanocrystalline TiO₂ films as electrodes in dye-sensitized solar cells is investigated and compared to nontreated films. As a result of this post-treatment cell efficiencies are improved, due to higher photocurrents. On a microscopic scale TiO₂ particle growth on the order of 1 nm is observed. Despite a corresponding decrease of BET surface area, more dye is adsorbed onto the oxide surface. Although it seems trivial to match this finding with the improved photocurrent, this performance improvement cannot be attributed to higher dye adsorption only. This follows from comparison between incident photon to current conversion efficiency (IPCE) and light absorption characteristics. Since the charge transport properties of the TiO₂ films are already more than sufficient without treatment, the increase in short circuit current density J_{SC} cannot be related to improvements in charge transport either. Transient photocurrent measurements indicate a shift in the conduction band edge of the TiO₂ upon TiCl₄ treatment. It is concluded that the main contribution to enhanced current originates from this shift in conduction band edge, resulting in improved charge injection into the TiO₂.

1. Introduction

Dye-sensitized solar cells based on nanocrystalline TiO₂ (DSC's) have attracted a lot of scientific and technological interest since their breakthrough in 1991.^{1–3} The setup and working principle of this type of solar cell is very different from solar cells based on p–n junctions in semiconductor materials (e.g. silicon, CIS). The functionalities of charge generation and transport are no longer combined in one material but separated in different materials, i.e., a sensitizing dye, a (wide band gap) semiconductor (TiO₂), and a liquid redox electrolyte. One of the advantages of this build-up is that charge recombination in the bulk is effectively suppressed in comparison to the situation in the classical p–n junction. As a result, the semiconductor material is allowed to have a much lower purity than is usual for semiconductor materials. Knowing this, in combination with a foreseen simple processing of devices, low production costs are expected.^{4,5} Although a low purity of TiO₂ can be tolerated, there are still opportunities for improvement of the properties of this material that is presently used in the DSC's.

A known method to improve the performance of the solar cells is a post-treatment of the TiO₂ film in which an extra layer of TiO₂ is grown onto the TiO₂ nanoparticles constituting the film. Different explanations of the working principle of this coating have been reported.^{6–9} These hypotheses concern increased surface area,⁶ improved electron transport,⁶ light scattering,⁷ TiO₂ purity,⁸ and dye anchoring.⁹ The post-treatment

has been carried out using several TiO₂ precursors and methods: TiCl₃ electrodeposition¹⁰ and titanium isopropoxide¹¹ and titanium tetrachloride (TiCl₄) post-treatment.^{6–9,12} The latter results in the highest efficiency increase for the solar cells.¹³

In this study the post-treatment of nanocrystalline TiO₂ films with TiCl₄ and its effects on the TiO₂ properties and solar cell performance have been investigated. The effect on the cell performance is revealed by an increase in incident photon to current conversion efficiency (IPCE) and short circuit current density (J_{SC}) of typically 10–30% relative to untreated films. The IPCE of a solar cell is influenced by three factors: light harvesting efficiency (LHE) of the colored TiO₂ film, electron injection efficiency (Φ_{INJ}) of the excited dye into the TiO₂, and the collection efficiency of the injected electrons to the TCO (Φ_{COLL}). The relation between these factors is given by

$$IPCE = LHE \times \Phi_{INJ} \times \Phi_{COLL}$$

Two of these three factors can be split up as follows in more detail:

LHE is resulting from TiO₂ surface area, dye loading, and light scattering/reflection events. Surface area is the total internal surface area of the TiO₂ film, and the dye loading is dependent on the number of specific binding sites on TiO₂ for the sensitizer. Light scattering influences the optical absorption of a film and can contribute to a higher performance.

Φ_{COLL} , the charge collection efficiency, is related to the ratio of charge transport through TiO₂ and charge recombination: $\Phi_{COLL} = K_t/(K_t + K_r)$, with K_t and K_r being the rate constants for transport and recombination, respectively.

In this study the observed increase in IPCE after TiCl₄ treatment has been investigated by analysis of these five factors: surface area, dye loading, light scattering, charge

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transport, and charge recombination. The first three factors will be considered in the sections about materials characterization and optical analysis of TiO₂ films (sections 3.1 and 3.2). Charge transport and recombination will be treated in the section about photoelectrical characterization of DSC (section 3.3).

2. Experimental Methods

2.1. Synthesis of Titanium Dioxide Colloids (TiO₂) and Preparation of Screen Printable Paste. TiO₂ colloids have been synthesized from titanium isopropoxide precursor according to procedures published earlier.¹⁴ In short, 58.6 g of titanium isopropoxide is mixed with 12 g of concentrated acetic acid and stirred for 15 min. The mixture is poured into 290 mL of water and stirred for 1 h. Then 4 mL of HNO₃ (65%) is added under stirring. The mixture is heated to 80 °C and stirred for 1.5 h at 80 °C under reflux. After cooling, the colloidal solution that has formed is transferred to a titanium autoclave and heated at 230 °C for 12 h. The TiO₂ colloid is transferred from the aqueous solution into a terpeneol/ethylcellulose mixture to obtain a screen printable paste using a pearl mill. TiO₂ films have been screen printed onto TCO-coated glass.

2.2. Fabrication of Solar Cells, Processing of Master Plates. Master plates have been applied as a research vehicle. A master plate consists of two SnO₂:F-coated glass plates (7.5 × 10 cm², LOF tec 8) on which five electrically isolated electrodes (area 4 cm²) are deposited by screen printing. One glass plate contains five TiO₂ photoelectrodes. To enhance the light absorption, an additional TiO₂ film consisting of 300 nm scattering particles (Fluka) has been applied to a part of the cells.^{6,15} The other glass plate contains five platinum (Pt) counter electrodes. The active layers (TiO₂ and Pt) are dried and fired at 570 and 450 °C for TiO₂ and Pt, respectively, to remove all organic components and to establish sufficient interparticle contacts between the TiO₂ particles. A typical film thickness of 10–12 μm TiO₂ is obtained after firing. The thickness of the light scattering film is typically 5 μm. The two glass plates comprising the photoelectrode and counter electrodes are laminated together using hotmelt foils such as Surlyn or Bynel. Further details are reported elsewhere.^{4,15–16}

For all experiments *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis(tetrabutylammonium) (N719, Solaronix S. A.) has been used as a sensitizer for TiO₂ electrodes. Solvents and additives hexylmethylimidazolium iodide (HMI, DSM), *tert*-butylpyridine (TBP, Aldrich), lithium iodide (LiI, Aldrich), guanidinium thiocyanate (Aldrich), and iodine (I₂, Aldrich) have been used as received without further purification.

The electrolyte used for performance and IPCE measurements consisted of 0.6 M HMI, 0.1 M LiI, 0.05 M I₂, and 0.5 M TBP in acetonitrile (ACN). For the cells tested in the transient measurements (section 2.7), the electrolyte compositions were as follows: electrolyte Gu, 0.6 M PMII, 0.1 M guanidinium thiocyanate, 0.05 M I₂, 0.5 M TBP in ACN; electrolyte Li, 0.6 M PMII, 0.1 M LiI, 0.05 M I₂, 0.5 M TBP in ACN; electrolyte HLi, 0.5 M LiI, 0.05 M I₂, 0.5 M TBP in ACN.

2.3. TiCl₄ Post-Treatment. The post-treatment with TiCl₄ has been applied to freshly sintered TiO₂ films according to literature procedures.¹² An aqueous stock solution of 2 M TiCl₄ was diluted to 0.05 M. Sintered electrodes were immersed into this solution and stored in an oven at 70 °C for 30 min in a closed vessel. After flushing with demineralized water and drying, the electrodes were sintered again at 450 °C for 30 min. For the determination of the increase in mass of the TiO₂ electrodes, a control group has been subjected to a similar

process, only leaving out the TiCl₄ in the dipping bath. The profiles and film thickness for TiO₂ films have been determined using a Dektak 8 stylus profilometer (Veeco Instruments).

2.4. Materials Characterization by XRD, TEM, and BET. XRD measurements have been conducted using Bruker D8 Advance equipment following the Bragg Brentano measurement method. TEM analyses were made using a JEOL 2010 transmission electron microscope operated at 200 keV with a LaB₆ filament. The TEM analysis of treated and untreated particles has been made by scraping off TiO₂ films and subsequently suspending them in a solvent. BET determination (single point BET) has been carried out using a Carla Erba Strumentazione, Sorpty 1750.

2.5. Optical Studies. Dye desorption experiments have been carried out using screenprinted TiO₂ films with and without TiCl₄ post-treatment. These films have been coated with N719 dye from a 0.3 mM ethanolic solution. For each sample the dye was desorbed from the electrodes by treating with a quantified amount of diluted (0.13 M) NH₃ in water, resulting in a dye solution of which a UV/vis (Hewlett-Packard 8453 UV/vis spectrophotometer) spectrum has been recorded. A correction for small variations (introduced by the screen printing process) in film thickness has been made by dividing the absorbance of each dye solution by the film thickness of each corresponding TiO₂ electrode. Since the absorbance is linearly related to the concentration of dye and for all samples the dye has been desorbed into equal volumes of diluted NH₃, the relative difference in absorbance directly translates into the relative difference in dye loading of the TiO₂ surface. Light absorption characteristics have been determined by reflection/transmission measurement using an integrating sphere.

2.6. IV and IPCE Characterization. IV measurements have been carried out using a Steuernagel constant 575 solar simulator (equipped with 575 W metal halide lamp) and a Keithley 2400 source meter. Calibration of this system has been carried out by comparative measurements of DSC's with a Spectrolab X-10 solar simulator. IPCE measurements have been carried out according to the ASTM E1021-84 norm.^{17–18} A 1000 W xenon lamp (Osram XBO/HS OFR) was used as a light source in combination with small band-pass filters (Schott, fwhm = 6–10 nm) to generate monochromatic light. The monochromatic light was passed through a chopper wheel to create a small modulated signal on top of a constant signal originating from 0.5 to 1 sun bias illumination. The resulting modulated current is analyzed by a lock-in amplifier.

2.7. Transient Photovoltage and Photocurrent Measurements. The effect of the TiCl₄ treatment on electron transport has been examined by measuring photocurrent transients under short circuit conditions. In these measurements, the bias light was modified to give approximately the same photocurrent for each cell, since the photocurrent transient is dependent on the magnitude of the photocurrent. Photocurrent and photovoltage transients were taken using a pump pulse generated by an array of red LEDs controlled by a fast solid-state switch. Pulse times of 100 μs were used, with a rise and fall time of <1 μs. The pulse was incident on the SnO₂ side of the cell. The pulse intensity was controlled to keep the ΔV due to the pulse below 10 mV. White bias light, incident on the SnO₂ side of the cell, was supplied by 10 W Solarc lamps (WelchAllyn). The bias light was attenuated when needed by neutral-density filters. The time resolution of the potentiostat was 20 μs; all transients were 200 μs or longer.

The transient voltage data have been used to calculate the capacitance at each V_{OC}. The procedure has been described

TABLE 1

Change of TiO ₂ Characteristics after TiCl ₄ Treatment						
	BET (m ² /g)	TiO ₂ mass ^a (mg/cm ²)	electrode surf. area ^b (m ²)	porosity ^c (%)	particle diameter (nm)	
					from TiO ₂ mass ^d	from TEM ^e
TiO ₂	72	1.56	0.449	70	na	13.1
TiO ₂ after TiCl ₄	53	2.00	0.424	63	na	15.7
change (%)	-26.4	+28	-6	-10	+8.6	+20
Change in IV Parameters after TiCl ₄ Treatment ^f						
	J _{SC} (mA/cm ²)	V _{OC} (V)	FF	η (%)		
TiO ₂	9.5 ± 0.2	0.68 ± 0.01	0.67 ± 0.004	4.3 ± 0.1		
TiO ₂ after TiCl ₄	11.2 ± 0.2	0.69 ± 0.01	0.66 ± 0.004	5.1 ± 0.1		
change (%)	+18	+1.5	-1.5	+19		

^a TiO₂ mass has been determined on 4 cm² electrodes and is expressed in mg/cm² geometrical electrode area. ^b Electrode (internal) surface area has been calculated by multiplication of BET and TiO₂ mass, for a 4 cm² film. ^c Porosity has been determined by calculating the overall density of a 4 cm² TiO₂ film from the TiO₂ mass, taking 13 μm film thickness and comparison to a density of 4.2 g/cm³ for bulk TiO₂. ^d Calculated from TiO₂ mass increase assuming spherical particles. ^e Particle diameters from TEM are based on measurement of diameters on TEM photographs (175 particles for each measurement). Statistic analysis reveals that the difference in particle diameter is significant at the 95% confidence level. ^f The IV measurements have been conducted on 4 cm² cells (without scattering layer) at a lamp intensity corresponding to 0.94 sun.

elsewhere.¹⁹ Briefly, the capacitance of the TiO₂/electrolyte interface can be calculated as $C = \Delta Q / \Delta V$, where ΔV is the peak of the transient and ΔQ is the number of electrons injected by the pulse. We find ΔQ by integrating a photocurrent transient at $V = 0$, caused by an identical pulse.

The following procedure was used to measure the recombination rate at short circuit.²⁰ The cell is placed under a given illumination. The attached potentiostat (galvanostatic mode) is set to supply a constant current equal to the short circuit current that the cell is generating. A light pulse is applied and the voltage transient that results is measured. When the constant current is set, a potential near $V = 0$ is maintained at the SnO₂ contact. When a light pulse is applied, the galvanostat must increase the voltage to counter the increase in current that would be caused by the increase in the photoinjected electron concentration in the porous TiO₂ film. Because the current and bias light are constant, the excess electrons can only leave the TiO₂ by recombination. The decay of the transient voltage thus measures the recombination rate relevant to short circuit current flow.

3. Results

3.1. Materials Characterization of the TiO₂ Films. The effects of the TiCl₄ treatment on TiO₂ films have been studied by BET, weight analysis, profilometry, XRD, and TEM. The results of these measurements are summarized in Table 1, also including the results of the IV measurements, as described in section 3.3.

Some obvious effects of the TiCl₄ treatment are a decrease in BET surface area and an increase in particle diameter and mass of the treated TiO₂ films. The average decrease in mass for the control group, which has gone through an equal process, only leaving out the TiCl₄ in the dipping bath, is 2.7%. This indicates that the measured increase in mass after the TiCl₄ treatment is significant and accurate. The small loss in mass of this control group can be attributed to a slight flaking of the

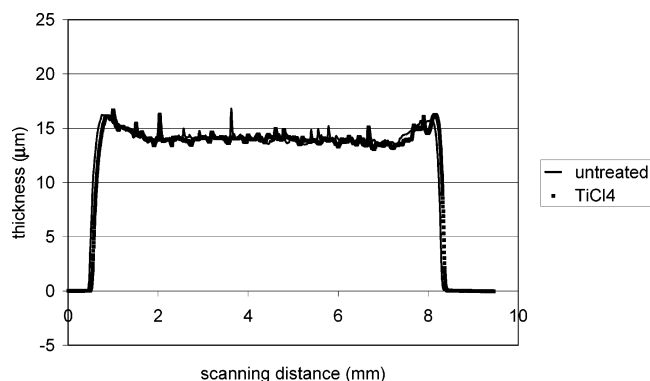


Figure 1. Profiles of TiO₂ films before and after treatment with TiCl₄.

TiO₂ film. To verify if the increase in TiO₂ mass is related to an increased TiO₂ film thickness, surface profiles of treated and nontreated films have been measured (Figure 1).

Comparison of the profiles indicates that, apart from occasional local TiO₂ clusters, no increase in TiO₂ film thickness results from the treatment, as is shown in Figure 1.

From these observations it follows that, despite the substantial decrease in BET surface area, the loss in actual electrode surface area after TiCl₄ treatment is only 6% (from 0.449 to 0.424 m²) because of the increase in mass of TiO₂ on the electrode. Since the film thickness is not affected, the porosity must have decreased, as is shown in Table 1.

From the increase in mass an increase in particle diameter of 8.6% has been calculated by assuming spherical particles, as shown in Table 1. From TEM measurements an increase in average particle diameter of 20% has been calculated.

No obvious difference can be seen between treated and untreated TiO₂ from the TEM photographs (Figure 2); however, by determination of a large number of particle diameters from the TEM photographs, a significant difference is observed, as follows from Figure 3 and is included in Table 1.

By X-ray diffraction an estimation of the primary particle size of the TiO₂ particles has been made. After TiCl₄ treatment the particle size is increased; the increase, however, could not be quantified. From XRD no obvious change in the rutile content (20–25%) of the TiO₂ could be observed, nor any other morphological changes; i.e., the formation of an amorphous phase or the presence of small crystallites was not observed.

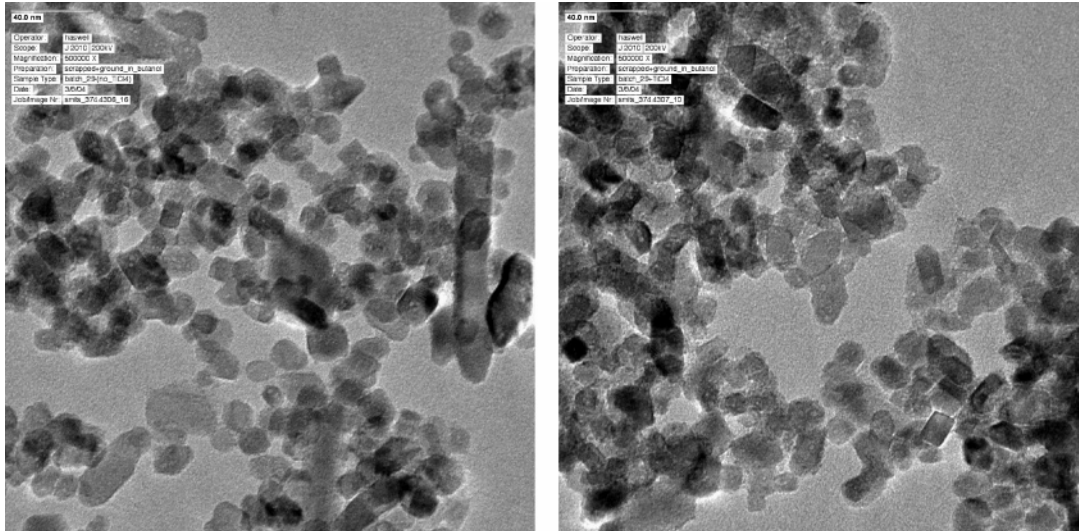
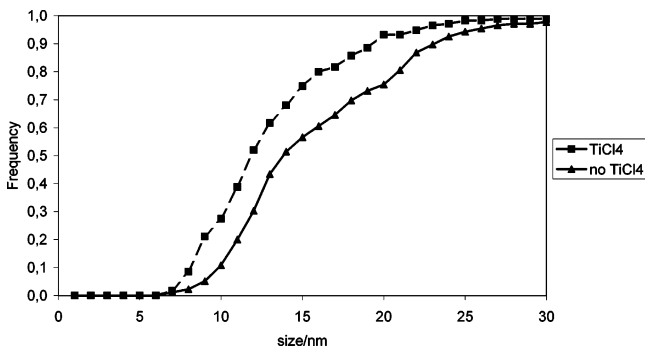
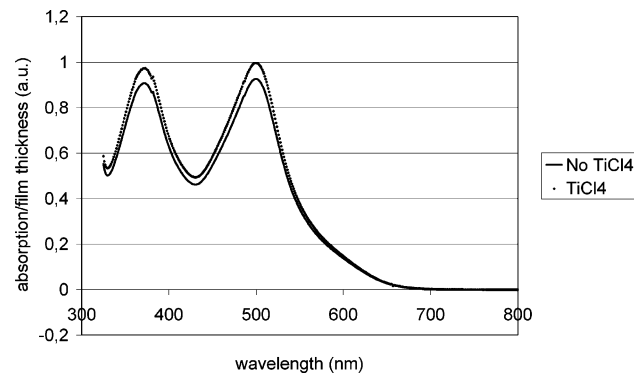
3.2. Optical Analysis of TiO₂ Films. For TiCl₄ treated and untreated TiO₂ films dye has been adsorbed and desorbed from the electrodes by treating with diluted NH₃, resulting in a dye solution of which a UV/vis spectrum has been recorded; see Figure 4.

The difference between TiCl₄-treated and nontreated TiO₂ is distinctive, showing a 7.6% higher dye loading for TiCl₄-treated electrodes.

To verify what is effectively changed in the TiO₂ film optical behavior by a higher dye load, optical analyses of colored TiO₂ films have been conducted using an integrating sphere (Figure 5).

The light absorption and reflection characteristics of colored TiO₂ films reveal that there is hardly any visible effect of the TiCl₄ treatment in the absorption maximum (550 nm) of the dye. This is because the light absorption is already saturated around this maximum, even without TiCl₄ treatment.

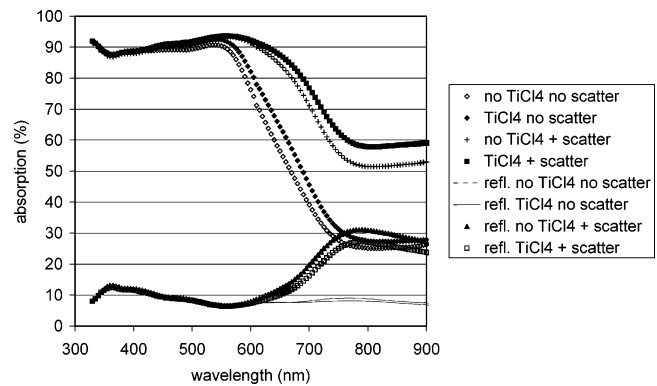
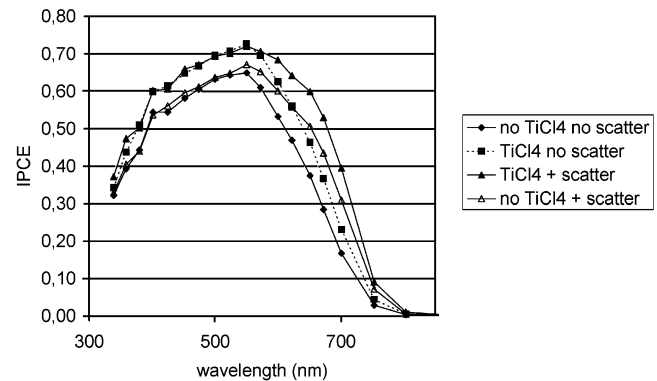
3.3. Photoelectrical Characterization of DSC. IV Characterization and IPCE Measurements. The beneficial effect of the TiCl₄ post-treatment on different IV parameters is presented in Table 1. The increase in current density and overall cell efficiency upon TiCl₄ treatment is 18% and 19%, respectively.

TiO₂ particles, magnification 500.000 timesTiO₂ particles after TiCl₄ treatment, magnification 500.000 times**Figure 2.** TEM photographs of TiO₂ particles with and without post-treatment with TiCl₄.**Figure 3.** Histogram of the particle distribution derived from the TEM photographs presented in Figure 2.**Figure 4.** Absorbance of aqueous dye solutions after desorption from TiO₂ films. The curves are normalized taking into account small differences in film thicknesses of the samples, originating from screen printing, by dividing the absorbance by the film thickness. Both curves represent the average of three samples. The difference in absorbance at 500 nm is 7.6% (± 0.07).

The increase in solar cell performance completely originates from the increase in current density; V_{OC} and FF are not affected.

To analyze in more detail the enhanced short circuit current, IPCE measurements have been conducted. The results are presented in Figure 6.

IPCE curves for TiCl₄-treated cells reveal an upward shift with respect to nontreated cells in the wavelength range from

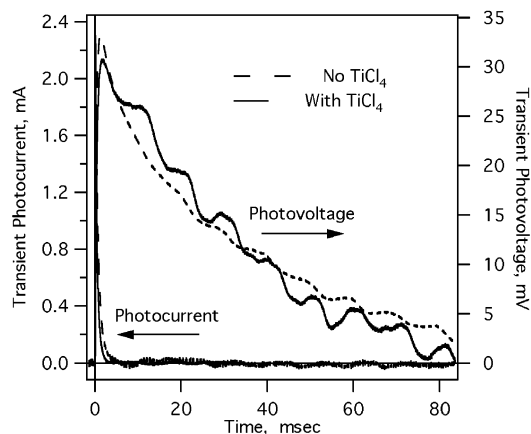
**Figure 5.** Light absorption of stained TiO₂ films (N719) with and without scattering layer and TiCl₄ treatment. The absorption has been derived from reflection transmission measurements using an integrating sphere. Reflection data have been added in the graph. Note: the nonzero absorption in the region from 800 nm onward is mostly due to the absorption of the TCO (in combination with the scattering properties of the films), as has been verified with noncolored films. The absorption maximum is approximately 93% because of a minimum reflection of 6–7% of the samples.**Figure 6.** IPCE curves of cells before and after TiCl₄ treatment with and without scattering layer.

350 to 800 nm, both for scattering and nonscattering films. The additional scattering layer induces an upward shift in the wavelength region between 550 and 800 nm, both for TiCl₄ treated and nontreated films. From the IPCE curves, J_{SC} has

TABLE 2: Electron Transport Time Compared with Steady State Photocurrent Increase for DSC with and without TiCl₄ Treatment

electrolyte	photocurrent transient half time (μ s) ^a		I_{PHOTO} increase (%)
	no TiCl ₄	TiCl ₄	
Gu	740	740	33
Li	880	680	28
HLi	950	910	26

^a Measured with white bias light intensity 70–90 mW/cm² varied to give identical steady-state current. Values are the average of two or three separate cells. Electrolyte compositions are described in the Experimental Section. Thin (3 μ m) TiO₂ layers were used in these cells to avoid RC limitation of the photocurrent transients; these thinner layers showed larger improvements from the TiCl₄ treatment than the thicker layers used for IV and IPCE measurements.

**Figure 7.** Transient photocurrent and transient photovoltage at short circuit for two matched cells with and without TiCl₄ treatment.

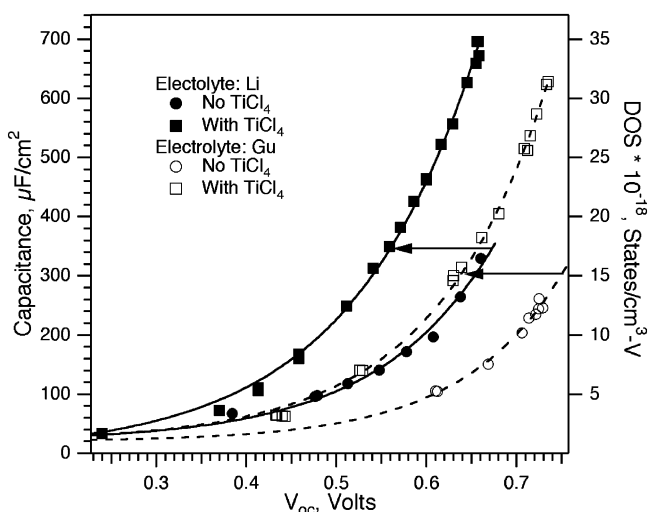
been calculated for these cells by convolution of the IPCE with the AM 1.5 G solar spectrum and subsequent integration. The deviation between these calculated values and measured J_{SC} under standard testing conditions (class A solar simulator, AM 1.5 G, 1000 W/m²) is small (0.7–3.2%). This shows that the IV and IPCE data are in good agreement.

Transient Photovoltage and Photocurrent Measurements. Transient measurements have been applied to examine charge transport and recombination. Table 2 shows the photocurrent transient lifetimes ($1/e$) for cells with and without TiCl₄ treatment and three different electrolytes. The change in 1 sun photocurrent for these particular pairs of cells is included.

As can be seen from Table 2, TiCl₄ treatment changes very little in the charge transport for two of the cases, and in the third case there was a 22% decrease in the transport time.

To further investigate the electron transport, we have compared the transport lifetime and the recombination lifetime under short circuit conditions. Figure 7 shows representative transport and recombination transients for a matched pair of cells, with and without TiCl₄.

The capacitance versus voltage of the cells with and without electrolyte was also measured. Figure 8 gives these results for two matched (with and without TiCl₄) pairs of cells. In each case a strong shift in the capacitance curve is apparent for the TiCl₄-treated cells. The capacitance of the TiO₂/electrolyte film is proportional to the differential density of states (DOS) at the Fermi level in the TiO₂ particles.^{19,21–22} The right axis on Figure 8 shows the DOS calculated for these films using $\text{DOS} = 6.24 \times 10^{18} \times C/(d(1-p))$, where C is the capacitance/cm², d is

**Figure 8.** Capacitance versus voltage of DSC with and without TiCl₄ treatment for two matched pairs of cells with different electrolytes.

the thickness of the TiO₂ film in cm, p is the porosity, and the conversion factor is the number of electrons per coulomb.

4. Discussion

As mentioned in the Introduction the IPCE of a DSC is a result of light harvesting efficiency (LHE), charge injection efficiency (Φ_{INJ}), and collection efficiency (Φ_{COLL}). For a given dye and absorption coefficient, LHE can be split into three contributing factors: surface area, dye loading, and scattering effects. Φ_{COLL} can be interpreted in terms of rates for transport (K_t) and recombination (K_r) in the following way: $\Phi_{\text{COLL}} = K_t/(K_t + K_r)$. The results described in the previous section will be discussed here in relation to these five factors.

4.1. Effects of the TiCl₄ Treatment on TiO₂ Morphology and Surface Area. The increase in photocurrent for TiO₂ layers that are treated with TiCl₄ in comparison to nontreated layers has led to speculations on increased dye adsorption due to an increase of the TiO₂ surface area.⁶ Also an increased layer thickness has been suggested as a reason for increased LHE.⁷ In the present investigation, it is shown that the net effect of the TiCl₄ treatment is a significant mass increase of the TiO₂ films with 28%. The TiCl₄ procedure does not influence the layer thickness, from which it can be concluded that all changes take place inside the film.

The only observable change in the X-ray diffraction pattern is line broadening, indicating particle growth. There are no indications that the TiCl₄ treatment results in the growth of small crystallites or an amorphous phase. This is supported by the decrease of the BET surface area. The TEM measurements indicate no morphological changes either. From the TEM recordings, particle growth from 13.1 to 15.7 nm is observed. The overall conclusion from these observations is that the TiCl₄ treatment leads to a growth of the TiO₂ particle radius of about 1 nm. The indications are that the growth is epitaxial.

The result of the TiCl₄ treatment is growth of the TiO₂ particles and a consequent decrease in BET surface area of about 26%. If the decrease in BET surface area (measured in m²/g) is combined with the increase in mass of 28%, this results in an overall decrease of the electrode surface area of approximately 6%. This means that the changes due to the TiCl₄ treatment on the TiO₂ morphology a priori do not provide any indications for the observed increase in photocurrent, since one would

expect a decrease of the electrode surface area to result in lower dye adsorption and decreased LHE.

4.2. Dye Adsorption and Photocurrent Generation. However, on the contrary, the effect of the TiCl_4 treatment does result in a distinctive increase in dye adsorption. The dye desorption experiments (Figure 4) show that the TiCl_4 -treated electrodes adsorb 7.6% more dye than the nontreated electrodes, despite the 6% lower surface area. The morphological studies do not provide data to accommodate this. This suggests that the reasons for the higher dye absorption are to be found on a different scale than can be seen with X-ray and TEM. Presumably, the TiO_2 surface after the TiCl_4 treatment provides more specific binding sites.¹³ Potentially, the TiCl_4 treatment also reduces the fraction of the TiO_2 surface area that is inaccessible for the dye due to sterical constraints.

The relation between more dye and more current seems obvious, and indeed, it has been reported to be the main reason for the observed increase in photocurrent due to the TiCl_4 post-treatment.^{6,8,12} However, a further analysis shows that only a part of the increase in photocurrent can be ascribed to the increased amount of dye, as is discussed below.

In Table 1, the IV data show that the increase in current due to the TiCl_4 treatment is 18%, whereas for these films a higher dye loading of 7.6% was observed (Figure 4). It is obvious that the increase in current is much more than can be ascribed due to the increase in dye loading. Moreover, the light absorption of films of this thickness is almost completely saturated in the absorption maximum of the dye, as was confirmed by determination of light absorption of the films (Figure 5). More dye in this case would not result in more current in the absorption maximum. It could only result in an improved red response, similar to what would happen if the layer thickness would be increased or if a scatter layer would be applied (see below).

To quantify this, the IPCE spectra of the cells were recorded. From Figure 6 it can be seen clearly that the IPCE curve shifts upward over the entire wavelength range upon the TiCl_4 treatment, as was also reported earlier.^{10,13} Further evidence comes from the IPCE measurements on similar layers but now equipped with an additional scatter layer on top. The effect of scattering clearly results in a much larger improvement of the red response than originates from the higher dye loading. Also for the films with scatter layer the entire IPCE curve is shifted upward. This upward shift in IPCE is 8% in the absorption maximum, which is in sharp contrast to a corresponding increase in light absorption of only 0.25%. It follows that other factors than the increased LHE play a role in the improved solar cell performance.

However, it should be noted that the enhanced photocurrents and IPCE values in the present study are lower than for the record cells,¹² so there is still opportunity for efficiency improvement.

In summary, although it is not expected on the basis of the observations discussed in section 4.1, the dye adsorption of TiO_2 is improved by TiCl_4 treatment. However, the photoelectrical analysis of the films shows that the contribution to an enhanced LHE is minor and the higher quantity of adsorbed dye is not the major contribution to the observed improvement in IPCE. This leaves Φ_{INJ} and Φ_{COLL} as candidates for IPCE improvement, as will be discussed in the next section.

4.3. Relation between Charge Transport, Recombination, and IPCE. As can be seen from the photocurrent transient lifetimes (Table 2), TiCl_4 treatment changes very little in the charge transport rate (K_t) for two cells. For the third cell, there was a 22% decrease in the transport time. Since the cells with

no change in transport show the largest improvement in photocurrent, it is apparent that, in general, an increase in electron transport is not the mechanism by which photocurrent was increased.

To further support this, we have compared the transport lifetime and the recombination lifetime under short circuit conditions. Figure 7 shows representative transport and recombination transients for a matched pair of cells, with and without TiCl_4 . It is clear from the transients that the transport under short circuit conditions is much faster than the recombination, and thus no losses to recombination are occurring at short circuit. More quantitatively, the recombination lifetime is about 40 ms, where the transport half times are about 900 and 700 μs . Under these conditions, about 2% of the charges are lost to recombination, so $\Phi_{\text{COLL}} = K_t/(K_t + K_r)$ is close to unity. Thus, even if large improvements in transport had been measured, they could not have been responsible for the increase in short circuit photocurrent observed. It can be concluded that Φ_{COLL} is not increased by the TiCl_4 treatment. This only leaves Φ_{INJ} as a candidate for improvement of IPCE/current. In the following sections this will be related to an observed shift in conduction band edge.

The density of states (DOS) versus voltage has been measured for cells with and without TiCl_4 . Figure 8 shows these results for two matched pairs of cells. In each case there is a strong shift in the DOS curve. The leftward shift along the V_{OC} axis is most likely the result of a shift of the TiO_2 band edge downward toward the I_3^-/I^- potential. The downward shift of the conduction band causes a given DOS to appear at a lower V_{OC} , as V_{OC} is measured up from the iodine/iodide potential. From the data, the magnitude of the shift is approximately 100 mV. Such a shift would imply that the surface potential of the TiO_2 is more positive in the cells with TiCl_4 treatment. This will cause a change in the surface dipole, to point more in the direction of the TiO_2 , moving the band edge down. The TiCl_4 treatment could cause this effect in several ways: For example, it may be that the crystal face exhibited by the TiCl_4 -treated TiO_2 is different from that expressed on the autoclaved particles. This could give rise to a stronger binding of protons and/or other cations. In any case, a 100-mV shift in the conduction band could be significant enough to increase the rate and the quantum efficiency of electron injection from the excited dye.

Alternatively, the shift in the DOS curves in Figure 8 could be viewed as an increase in the trap density rather than a shift of the conduction band. Interpreted in this way, the TiCl_4 treatment increases the trap density by a factor of ~ 2.3 across the whole voltage range. Several factors argue against this interpretation. Since the TiCl_4 treatment only increases the TiO_2 mass by a factor of 1.4, an overall increase in traps of a factor 2.3 would imply that the TiCl_4 deposited TiO_2 has a trap state density that is 3.5 times higher than the original TiO_2 particles, which is unlikely. Moreover, such a large increase in trap density would be expected to slow the transport, which is not observed, and to increase the amount of charge stored in the film under short circuit conditions, which is also not observed. A shift in band edge is the most probable explanation. Further discussion of this question will be given in a coming paper.²³

It may be noted that a downward shift in the conduction band should give a lower V_{OC} . This does not occur because the TiCl_4 treatment also acts to strongly reduce the recombination rate. This has been mentioned in the literature, and we have confirmed a 30-fold reduction in the recombination rate for a given DOS in the cells used in this study.^{23–24} The reduction in the recombination rate allows the 1 sun flux of injected

electrons to build up a higher density of charge in the TiO₂ (see Figure 8). This effect compensates for the downward movement of the band edge.

5. Conclusions

Our observations show an increase in photocurrent that is primarily not caused by an increase in light absorbed or by a decrease in losses during transport. From this we can conclude that, in the untreated films, some absorbed photons do not result in electron injection into the TiO₂ conduction band. Our data do not preclude that some electrons are injected into surface states, which then recombine geminately with the dye. One explanation for some excited dye molecules failing to inject would be a conduction band potential that was near or above the oxidation potential of the excited dye. In this case, the electron injection rate could be slow enough that other reactions can compete with injection to some extent. Under this explanation, a downward shift in the band edge would be expected to give a higher quantum efficiency of injection and thus a higher photocurrent, as observed.²⁵

It is also interesting to note that the efficacy of the TiCl₄ treatment has been found to vary widely, depending on the source and history of the particles used to make the film. This would be expected if the source of the increased photocurrent is a shift in the band edge. If, for a given particular film, the band edge was already at the correct potential to maximize the quantum efficiency of injection, then further shifts caused by the TiCl₄ treatment would not be beneficial. In other words, when the photocurrent is already high without the treatment (corresponding to cell efficiencies around 10%), the improvements with TiCl₄ are limited.¹²

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