Improved Performance of Quasi-solid State Dye-Sensitized Solar Cells After Photoanode Surface Treatment with Novel Materials

D. Sygkridou, A. Rapsomanikis, A. Apostolopoulou, A. Ifantis and E. Stathatos

Abstract At the present work, we investigate the effect of TiO_2 nanocrystalline films surface treatment with two titanium based organic materials using chemical bath deposition technique. The two novel materials are titanium(IV) (triethanolaminato) isopropoxide and titanium(IV) bis(ammonium lactate)dihydroxide which are structural different from $TiCl_4$ which is a common material for TiO_2 post-treatment. The treated and untreated films are examined as negative photoelectrodes in quasi-solid state dye sensitized solar cells. The cells were characterized in terms of their electrical characteristics while direct comparisons based on the structural properties of the films were also made. Both treated films as photoelectrodes in dye sensitized solar cells exhibited better performance compared to the untreated films with recorded 26–30 % increase to the overall efficiency depending on the material used for the treatment. Dark current measurements were also performed in order to evaluate the effect of both materials as reducers of charge recombination rates.

Keywords Dye sensitized solar cells · Nanocrystalline materials · Photoelectrode treatment

1 Introduction

Over the past decades dye sensitized solar cells (DSSCs) have attracted intense interest mainly owing to the simplicity of their fabrication procedures, practically under ambient conditions with mild chemical processes and the fact that it is

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possible to manufacture transparent cells that can be used in a variety of applications [1–3]. Although the overall efficiency has reached the record efficiency of 12 % (for laboratory small size) there is still space for further improvements at different fabrication steps of cells realization [4]. In order for DSSCs to become a commercially attractive alternative to conventional photovoltaic solar cells, improvements concerning their cost, overall efficiency and long-term stability are required. In particular, the control of the quality, morphology and design of the mesoporous titanium dioxide as basic photoanode material is of high interest among suggested improvements [5–7].

To enhance the DSSCs performance, the recombination rate, which is considered to be responsible for the dark current and represents the major source of current loss, needs to be reduced [8]. Therefore many researcher's attention has been focused to finding ways to achieve a better contact between the conductive glass (SnO_2:F) and the semiconductor used to manufacture the DSSC and suppress the charge recombination. Throughout the literature there is evidence that an additional layer covering the TiO_2 surface can block the recombination of conduction band electrons with the oxidized dye molecules or the redox system at the TiO_2/electrolyte interface, increasing the photocurrent [9–11]. A widely known procedure to improve the efficiency of the cells is the treatment of the conductive FTO substrate and TiO_2 mesoporous film with an aqueous solution of $TiCl_4$. However, except the use of $TiCl_4$ as a basic material for surface treatment of TiO_2 electrodes many studies have focused on the interface controlling of TiO_2/electrolyte to reduce the loss of the generated electrons especially by introducing Al_2O_3, Nb_2O_5 and $SrTiO_3$ for surface modification of mesoporous electrode [12–14]. The pre-treatment enhances the bonding strength between FTO substrate and porous TiO_2 film while blocks the charge recombination between electrons at FTO and electrolyte. However, the treatment of TiO_2 mesoporous film also improves the connection between nanoparticles and finally increases the current at the cells.

In this work, we demonstrate that the cell's overall efficiency can be enhanced by TiO_2 particles' surface treatment. The TiO_2 nanocomposite films are dipped in a sol containing the surface modifier molecules and stayed for short time succeeding the particles coverage according to chemical bath deposition technique. We studied the effect of two different solutions of (Titanium(IV) (triethanolaminato) isopropoxide (TTAI) and Titanium(IV) bis(ammonium lactate)dihydroxide (TALD) to the short circuit current density, open circuit voltage, fill factor and overall efficiency of quasi-solid state dye sensitized solar cells and finally the results were compared with differences monitored at the structural properties of the films. The TiO_2 films treated with the two aforementioned titanium precursors using chemical bath deposition method showed an increase to their electrical performance under full sunlight exposure. Treated cells with the new precursors are compared with reference cells without TiO_2 particle surface treatment to determine which electrical parameters are most affected. The effect of the annealing temperature of the treated films is also examined.

2 Experimental Section

2.1 Materials

Commercially available lithium iodide, iodine, 1-methyl-3-propylimidazolium iodide, guanidine thiocyanate, chloroplatinic acid hexahydrate (H_2PtCl_6), poly (propylene glycol) bis(2-aminopropyl)ether, 3-isocyanatopropyltriethoxysilane and all solvents were purchased from Sigma-Aldrich and used as received. Titanium (IV) (triethanolaminato) isopropoxide, 80 wt.% solution in 2-propanol and Titanium(IV) bis(ammonium lactate)dihydroxide, 50 wt.% solution in water were also purchased from Sigma-Aldrich and were further diluted using their solvent until their concentration was 1 M. 3-*Cis*-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) bis(tetrabutylammonium), N719 was purchased from Solaronix S.A, Switzerland. SnO_2:F transparent conductive electrodes (FTO, TEC15) 15 Ohm/square were purchased from Hartford Glass Co., USA. Commercial ultrapure titanium isopropoxide (TTIP, 97 %, Aldrich), Triton X-100 (polyethylene glycol p-tert-octylphenyl ether) surfactant (99.8 %, Fisher Scientific), glacial acetic acid (AcOH, Aldrich) were used to make precursor TiO_2 sols and form a blocking layer among FTO and TiO_2 paste. Titania powder P25 was provided by Degussa, (Germany, 30 % Rutile and 70 % Anatase).

2.2 Preparation of TiO₂ Photoanodes Sensitized with Dye

TiO_2 thin films were first deposited on FTO glasses as blocking layers by following a previously reported procedure [15, 16]. Briefly, for 5.4 ml solution, 0.72 g of Triton X-100 were mixed with 4 ml of ethanol, followed by addition of 0.4 ml of glacial acetic acid and 0.32 ml of titanium isopropoxide under vigorous stirring. After a few minutes stirring, FTO glasses were dipped in the above sol and withdrawn with 2 cm/s. The films were heated up to 500 °C for 30 min using 20 °C/min heating ramp rate. The procedure was applied for the deposition of only one TiO_2 layer while the film thickness was approximately 150 nm. Then a layer of TiO_2 paste was deposited by doctor blading followed by heating to 500 °C. The fabrication of TiO_2 paste is as follows: 3 g of Degussa P25 was mixed with 0.5 ml of acetic acid in a mortar for about 3 min. After that, 2.5 ml of Millipore water and 17.5 ml of ethanol were alternately added to break all TiO_2 aggregates and form a homogenous solution. The solution was transferred to a crucible with 50 ml of ethanol and was mixed with 10 g of terpineol and an amount of ethyl cellulose. The solution was ultrasonicated for about 2 min and then the crucible was placed in a rotary evaporator at 40–45 °C to remove the excessive solvent and form the TiO_2 paste.

After cooling down at around 100 °C, some of the glasses were dipped for 30 min either to the 1 M Titanium(IV) (triethanolaminato) isopropoxide solution

(a)   **(b)**
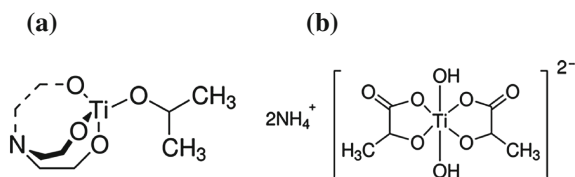
Scheme 1 **a** Titanium (IV) (triethanolaminato) (TTAI) and **b** Titanium(IV) bis(ammonium lactate)dihydroxide (TALD)

(hereafter denoted as TTAI) or to the 1 M Titanium(IV) bis(ammonium lactate) dihydroxide (hereafter denoted as TALD) with two different annealing temperatures (hereafter denoted as i.e. TTAI-300, TTAI-500 and meaning that the films were dipped in 1 M Titanium(IV) (triethanolaminato) isopropoxide solution and sintered at 300 and 500 °C respectively). The chemical structures of TTAI and TALD appear in Scheme 1. The cells fabricated with these glasses were compared with cells with photoanodes that weren't dipped in any of the above solutions (hereafter denoted as reference). BET measurements were performed to determine the pore size distribution, the pore volume and the films' porosity and they were conducted with Micromeritics Tristar 3,000 while film morphology and film thickness were characterized by Scanning Electron Microscopy (FE-SEM, FEI Quanta) and Veeco profilometer respectively. Finally, all the TiO_2 films were immersed in an ethanol/ acetonitrile (1/1 v/v) solution of N719 (the dye concentration was 5×10^{-4} M) in order to sensitize the TiO_2 electrode in the visible region.

2.3 Fabrication and Characterization of Quasi-Solid Dye-Sensitized Cell

In the construction of the solar cells a quasi-solid state electrolyte was used. This was chosen as a promising approach to DSSC technology as it combines the high ionic conductivity of liquids while it reduces the risk of leaks and minimizes sealing problems in the cells. For the gel electrolyte applied to the DSSCs, we used a hybrid organic-inorganic material which was prepared according to a procedure described in previous publications [17, 18]. Briefly, poly(propylene glycol) bis(2-amino-propylether) of molecular weight 230 and 3-isocyanatopropyltriethoxysilane (ICS; molar ratio ICS/diamine = 2/1) react in a vessel (acylation reaction), producing urea connecting groups between the polymer units and the inorganic part. The gel electrolyte was synthesized by the following procedure: 0.7 g of the functionalized alkoxide precursor (hereafter ICS-PPG230) were dissolved in 1.6 g of sulfolane and 0.8 g of methoxypropionitrile under vigorous stirring. Then, 0.6 ml AcOH were

added followed by 0.3 M 1-methyl-3-propylimidazolium iodide, 0.1 M LiI and 0.05 M I_2 in a final molar ratio AcOH:LiI:MPImI:I_2 = 2.5:0.1:0.3:0.05. After 6 h stirring, one drop of the obtained sol was placed on the top of the titania electrode with adsorbed dye molecules and a slightly platinized FTO counter electrode was pushed by hand on the top. The platinized FTO glass was made by casting a few drops of a H_2PtCl_4 solution (5 mg/1 ml of ethanol) followed by heating at 450 °C for 10 min. The two electrodes tightly stuck together by Si–O–Si bonds developed by the presence of the hybrid material.

2.4 Characterization of the DSSCs

For the *J-V* curves, the samples were illuminated with Xe light using a Solar Light Co. solar simulator (model 16S-300) equipped with AM 0 and AM 1.5 direct Air Mass filters to simulate solar radiation at the surface of the earth. The light intensity was kept constant at 1,000 W/m^2 measured with a CMP 3 Kipp and Zonen pyranometer. Finally, the *I-V* curves were recorded by connecting the cells to a Keithley Source Meter (model 2601A) which was controlled by Keithley computer software (LabTracer). The cell active area was constant to 0.3 cm^2 using appropriate mask while back reflectors were not used in the measurements. For each case, we made two devices which were tested under the same conditions in order to avoid any misleading estimation of their efficiency. Cell performance parameters, including short-circuit current density (J_{SC}), open circuit voltage (V_{OC}), maximum power (P_{max}), fill factor (*FF*) and overall cell conversion efficiency, were measured and calculated from each *J-V* characteristic curve. Two devices were prepared for each case of TiO$_2$ surface modifier (Titanium(IV) (triethanolaminato) isopropoxide sintered at 300 and 500 °C) and (Titanium(IV) bis(ammonium lactate)dihydroxide sintered at 300 and 500 °C).

3 Results and Discussions

TiO$_2$ films are fabricated in two steps before their treatment with the two different structured titanium precursors. A thin layer of TiO$_2$ on FTO glass substrates was applied via sol-gel method while a second thicker layer was coated on top of the above layer made of nanocomposite TiO$_2$ paste using P25 commercial powder by doctor blade technique. The final thickness of the film was approximately 4 μm according to profilometer measurement. After the preparation of the two different layers of TiO$_2$, the films were dipped in 1 M titanium(IV) (triethanolaminato) isopropoxide solution in isopropanol or to a 1 M Titanium(IV) bis (ammonium lactate)dihydroxide in water followed by heating either to 300 or 500 °C. The final thickness of the TTAI or TALD treated films were approximately 3.7 and 3.8 μm respectively. The SEM images of treated and untreated films are presented in Fig. 1.

Fig. 1 SEM images of:
a pure P25-TiO$_2$, **b** TTAI
modified P25-TiO$_2$ and
c TALD modified P25-TiO$_2$
films sintered at 500 °C
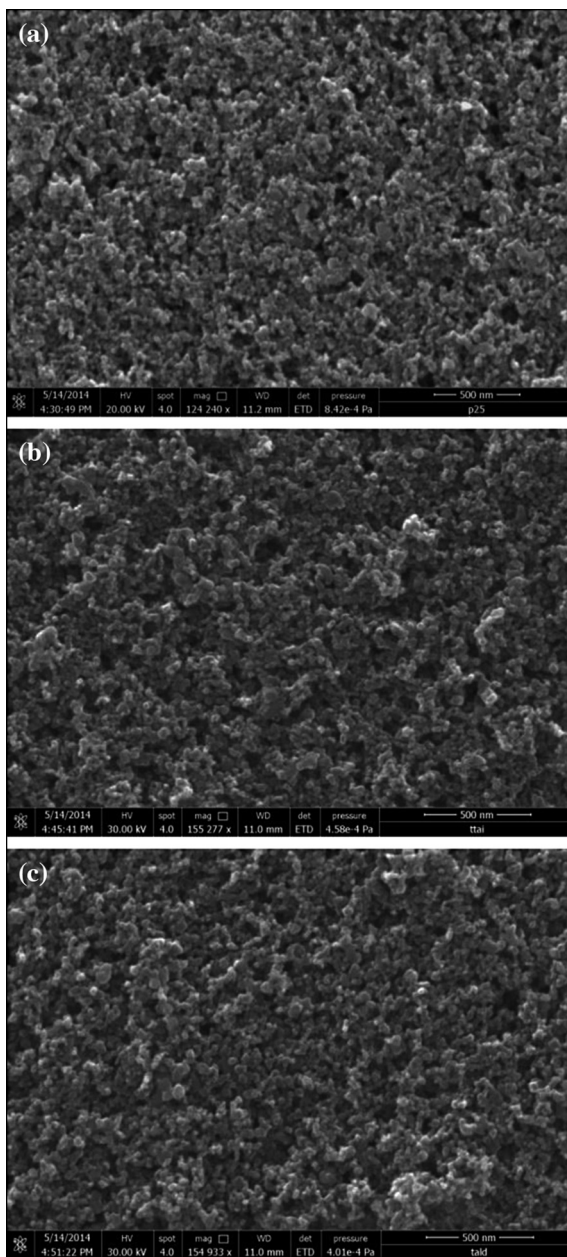
As it can be seen the untreated film is consisted of nanoparticles with an average
size of 25 nm as it was expected because of the use TiO$_2$-P25 as starting material.
However, no serious deviations are displayed in the presence of TTAI or TALD
after films' treatment. The homogeneity of the films and the particle average size
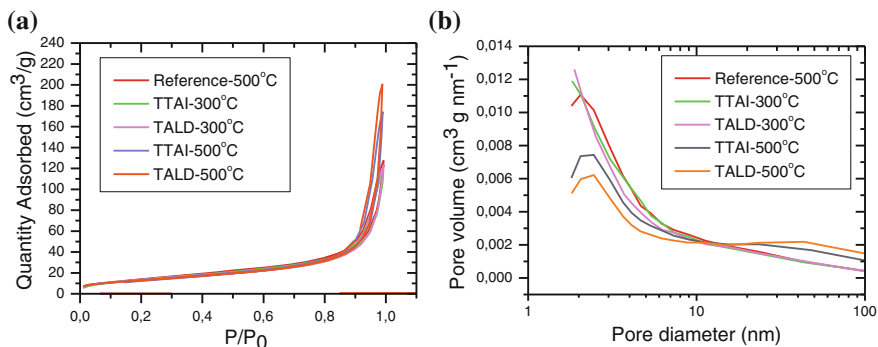
(a)

(b)

Fig. 2 Sorption-desorption isotherms **a** and pore size distribution **b** for treated and untreated TiO$_2$ films

look similar among the three images of Fig. 1. This means a very thin coverage of TiO$_2$ particles in films which does not affect to the increase of the total thickness of the film and particle size. Finally, TTAI and TALD treated TiO$_2$-P25 films look more porous than untreated films, therefore porosimetry measurements were performed to estimate structural properties of all films.

The texture of untreated P25 powder based nanocrystalline films and TTAI, TALD treated were analyzed by N$_2$ adsorption and desorption. The results are shown in Fig. 2a, b. In addition, their BET surface area and pore structure are also summarized in Table 1. From Fig. 2a, the hysteresis loop appear in relatively high pressure region (0.8 < P/Po < 1.0), which suggests that Degussa P25 particles could lead to the formation of larger pores. For treated and untreated TiO$_2$ matrix leads to the formation of enhanced mesopore structure. Moreover, treated samples seem to exhibit relatively wider pore size distribution (22–26 nm) compared to the untreated and treated at lower temperature samples (14–15 nm). This behavior to the pore size distribution affects the porosity and total pore volume of the samples which are at the same order. Such large pores are expected to have a beneficial effect on the electrolyte solution wetting and filling in the TiO$_2$ films. However, the specific surface area of particles is lower in the case of treated samples heated at 500 °C. From Table 1, it can be seen that the BET surface area of the untreated TiO$_2$ films is 53.01 m^2/g which is getting lower $\sim$51 m^2/g for treated TiO$_2$ films at 300 °C. Finally the surface area is getting even lower 47–48 m^2/g for treated samples at 500 °C. However, the difference between untreated and treated samples at 500 °C is only 11 %. Finally, as the specific surface area decreased after surface treatment the roughness factor of the treated films was also decreased (500 °C) after compared with the value of the untreated samples.

Figure 3 shows the absorbance of N-719 dye after detachment from all TiO$_2$ films exposed to 1 M NaOH for the same time (10 min). It is obvious that the quantity of the dye detached from all treated samples is higher than the untreated sample. The exact intensity of the dye's absorbance at both wavelengths in the

Table 1 Structural characteristics of treated and untreated TiO$_2$ films

Sample	Pore size (nm)	Porosity, P (%)	Total pore volume, Vp (cm^3/g)	Specific surface area, S (m^2/g)	Roughness factor (μm^{-1})[a]
Reference	14.86	0.43	0.197	53.01	2.43
TTAI-300	13.99	0.41	0.181	51.67	2.09
TALD-300	14.96	0.42	0.191	51.01	2.76
TTAI-500	22.14	0.50	0.269	48.57	1.76
TALD-500	26.32	0.54	0.310	47.11	2.37

[a] roughness factor was obtained by multiplying the specific surface area and TiO$_2$ weight

Fig. 3 UV-Vis absorption of dye N-719 detached from untreated and TTAI, TALD treated TiO$_2$ nanocrystalline films after exposition in 1 M NaOH
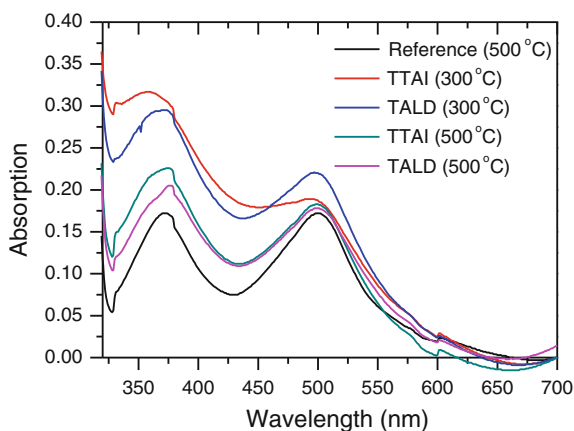

visible is presented in Table 2. TTAI, TALD surface treatment of TiO$_2$ films increased the amount of adsorbed dye. This may be caused due to passivation of TiO$_2$ surface and increased pore size distribution, pore volume and porosity of the films. The effect of higher adsorbed amounts of dye on TiO$_2$ films' surface was examined in the performance of DSSCs constructed in quasi-solid state electrolyte configuration.

The current-voltage (J-V) characteristic curves of quasi solid-state dye sensitized solar cells for all TiO$_2$ films are presented in Fig. 4. As it can be seen the quasi-solid state DSSCs constructed with untreated and treated TiO$_2$ films showed different energy to power conversion efficiencies under AM 1.5 simulated Xe-light of 100 mW/cm^2. In the case of TALD treated TiO$_2$ film the overall efficiency was slightly higher than the case of TTAI surface treated TiO$_2$ film. In particular, the open circuit voltage for TALD treated sample was 0.71 V and the short circuit current was 8.35 mA/cm^2. The overall efficiency for this cell was measured 4.04 %. For the cell containing TALD treated photoelectrode, with exactly the same electrolyte

Table 2 Absorbance of N-719 dye after detachment from TiO$_2$ films

Sample (°C)	Wavelength (nm)	Absorbance
Reference (500)	372.5	0.173
	500.5	0.171
TTAI-300 (300)	356.5	0.316
	490.5	0.191
TALD-300 (300)	371.5	0.294
	497.0	0.219
TTAI-500 (500)	374.5	0.183
	499.0	0.226
TALD-500 (500)	377.0	0.205
	499.0	0.178

Fig. 4 Photocurrent-voltage curves of DSSCs based on treated and untreated TiO$_2$ nanocrystalline films
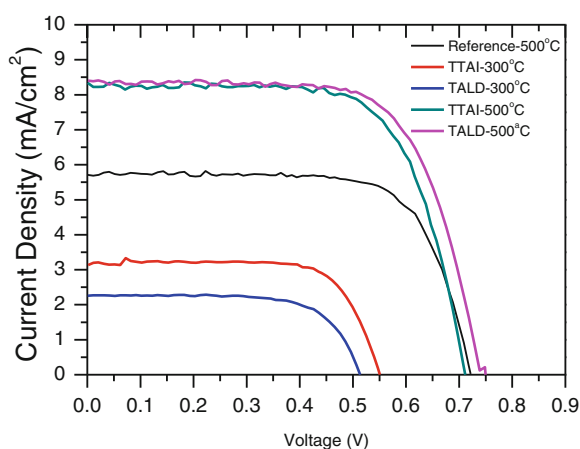
composition, the open circuit voltage was measured 0.74 volts and the short circuit current was 8.42 mA/cm^2. The overall efficiency for this cell was slightly increased to 4.25 %.

In both cases, the active area of the cells was 0.3 cm^2. We attribute the difference in overall efficiencies of the cells to the different textural and morphological characteristics of the two films as they were described in this section. Specifically, the difference may be explained by the higher number of active sites for the adsorption of dye molecules, the larger average pore size for effective mass transfer of electrolyte and light harvesting.

It is worth of noting that the efficiency of the untreated TiO$_2$ sample is much lower (2.97 %) mainly caused from lower recorded current density.

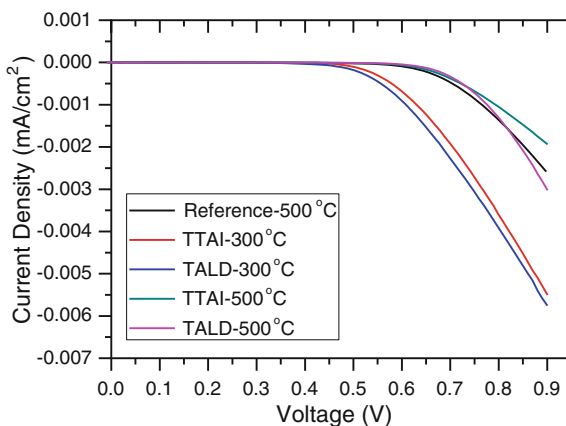**Fig. 5** Dark current-voltage characteristic curves of dye-sensitized solar cells before and after TTAI, TALD treatment

Table 3 Solar cells parameters for DSSCs with TTAI, TALD treated or untreated TiO_2 photoelectrodes

Sample (°C)	J_{SC} (mA/cm^2)	V_{oc} (V)	FF	n (%)
Reference (500)	5.71	0.72	0.721	2.97
TTAI-300 (300)	3.11	0.55	0.753	1.29
TALD-300 (300)	2.26	0.51	0.693	0.80
TTAI-500 (500)	8.35	0.71	0.683	4.04
TALD-500 (500)	8.42	0.74	0.684	4.25

Consequently, a 26.5 and 30.1 % increase to the overall efficiency was recorded for the TTAI and TALD treated photoanodes respectively. Finally, the treated samples heated at lower temperature (300 °C) exhibited poor performance mainly due to the carbon content which is still present as the temperature exposed the films was not enough elevated to remove carbon. The TiO_2 treated samples were also examined as efficient photoelectrodes in DSSCs measuring the dark current suppression. Figure 5 shows that the electron leakage, in the cells made with TTAI, TALD surface treated TiO_2 films at 300 °C is noticeably higher compared to the cells with untreated and TTAI, TALD treated TiO_2 films at 500 °C which leads to a reduced overall performance under light exposure (Table 3).

Among untreated and treated with TTAI, TALD photoelectrodes but all heated up to 500 °C it is monitored a very slight performance in case of the presence of TTAI.

4 Conclusions

Two titanium based materials were used for TiO_2 mesoporous films surface treatment. The treated and untreated films were examined as photoanodes in dye sensitized solar cells and their performance was evaluated in terms of photocurrent,

photovoltage and overall efficiency. Differences to their performance were attributed to the different structural properties and different recombination rate of the carriers in the films. In particular, the treated films with Titanium(IV) (triethanolaminato) isopropoxide and Titanium(IV) bis(ammonium lactate)dihydroxide were exhibited more porous structure and roughness while the amount of the absorbed dye was higher compared to the untreated samples. Finally, 26–30 % increase to the overall performance of the cells with TTAI and TALD treated photoanodes was measured.

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