Modification of fluorine-doped tin oxide-electrodes by electrochemical reduction of di(4-nitrophenyl)iodonium tetrafluoroborate - And its application as a photo-anode in dye-sensitized solar cells

Christiansen, Cathrine D.; Sørensen, Lars A.; Lund, Torben

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Cathrine D. Christiansen, Lars A. Sørensen, Torben Lund[*]

Department of Science and Environment, Roskilde University, DK-4000, Denmark

*Corresponding author: Tel.: +45 46742472, Fax: +45 46733011, E-mail address: tlund@ruc.dk

(Torben Lund)

Abstract

We report on a straightforward methodology to cover the FTO layer of the DSC photo anode with an insulating layer of nitro phenyl groups by electrochemical reduction of di(4-nitrophenyl)-iodonium tetrafluoroborate **1**. The efficiency of the blocking layer was demonstrated by a ferrocene CV test, in which ferrocene CV peak separations increased from 200 to 400 mV, and in which the charge transfer resistance measured by EIS increased from 600 to 20.000 Ω depending on the number of grafting CV scans. Our DSCs displayed a V_{oc} increase of 182 mV at 90 W/m^2 corresponding to a reduction in the dark current with a factor of 1000, when using D5 as sensitizing dye, $[Co(bipy)_3]^{2+/3+}$ as mediator, and FTO│TiO$_2$ as an electrode that had been grafted before by three CV scans of **1**. However, DSCs prepared with N719 and D35 as dyes and using FTO│TiO$_2$ as photoanode grafted with **1** showed decreased performance on all cell parameters.

1. Introduction

Dye-sensitized solar cells (DSCs) as well as its solid-state version (SSDSC) are low cost alternatives to traditional silicon solar cells [1-5]. So far however, the light-to-energy efficiencies of DSCs and SSDSC are too low in order to rival with existing silicon solar cells. One strategy to increase the efficiency of DSCs is based on preventing the dark current of the cell. After injection of an electron from the excited state of the dye into the mesoporous TiO_2 network the electron moves to the fluorine-doped tin oxide (FTO) back contact and from there into the outer circuit. The dark current is caused by unwanted spontaneous loses of electrons from the FTO surface as illustrated in Figure 1.
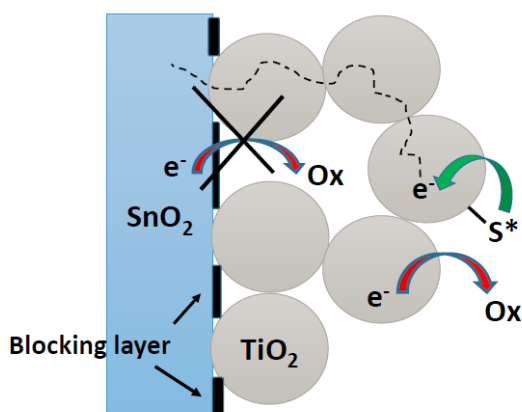
Figure 1 Mechanism of the undesired back electron-transfer, and strategy to minimize the loss of electrons. Dotted line: back electron-transfer by spontaneous loses of electrons from the FTO surface

The leaking of electrons causes a) the undesired electron transfer to the oxidized form of the dye (S^+) with formation of the reduced dye (S) and (b) the undesired reduction of the oxidized form of the redox mediator/hole conductor [6]. The dark current is a problem especially for DSCs applying one-electron mediators such as $[Co(bipy)_3]^{2+}/[Co(bipy)_3]^{3+}$, ferrocene/ferrocenium or hole conductors, whereas the dark reaction is of less importance in DSCs applying two-electron mediators such as I^-/I_3^- [7-9]. The relative ratio between the dark current from FTO$|$TiO$_2$ surfaces is not well

investigated and the best strategy to prevent these undesired back electron transfers would be to cover both, the FTO and the TiO_2 surface, with an electrically insulating layer. In this paper we will report our results of protecting the FTO surface (see Figure 1).

The predominant strategy to minimize the dark current from the FTO is based on coating the surface with a very compact blocking layer of TiO_2 particles, and the application of a meso-porous TiO_2 layer on top of the compact layer. The TiO_2-blocking layer has been prepared by spray pyrolysis [10], electrodepositions [11], atomic layer deposition (ALD) [12, 13] or $TiCl_4$ treatment [14, 15]. All these methods require a sintering step at elevated temperatures of 450-500 ˚C, and thus preclude the preparation of DSCs based on flexible plastic substrates coated with FTO. In this respect, there is a clear need for low-temperature FTO blocking layer fabrication methods.

Gregg *et al*. introduced in 2001 an electrochemical method to cover the FTO part of the photo anode by an organic insulating layer of phenol/2-allylphenol copolymer, and demonstrated functional DSCs with ferrocene/ferrocenium as mediator [16]. The layer was electrochemically grafted as illustrated on Figure 1 on the free FTO spaces between the TiO_2 particles. Coating the empty FTO areas with an organic insulator should not hinder the injected electrons from reaching the FTO back contact. Recently, we have applied a similar strategy, in which $SnO_2|TiO_2$ photo anodes were electrochemically grafted with a layer of nitrophenyl groups in a solution of nitrophenyldiazonium ions [17]. However, the problem of this grafting method is the difficulty to avoid the formation of multilayers. Thinner and more controllable layers may be formed by the reduction of iodonium salts, which are less prone to produce multilayers as diazonium salts [18].

Scheme 1 shows our grafting strategy for the protection of a FTO surface by the reduction of iodonium salts. Very recently Charlton *et al*. [19] have suggested a mechanism for the grafting of indium doped tin oxide by reduction of di(4-nitrophenyl) iodonium tetrafluoroborate ion.
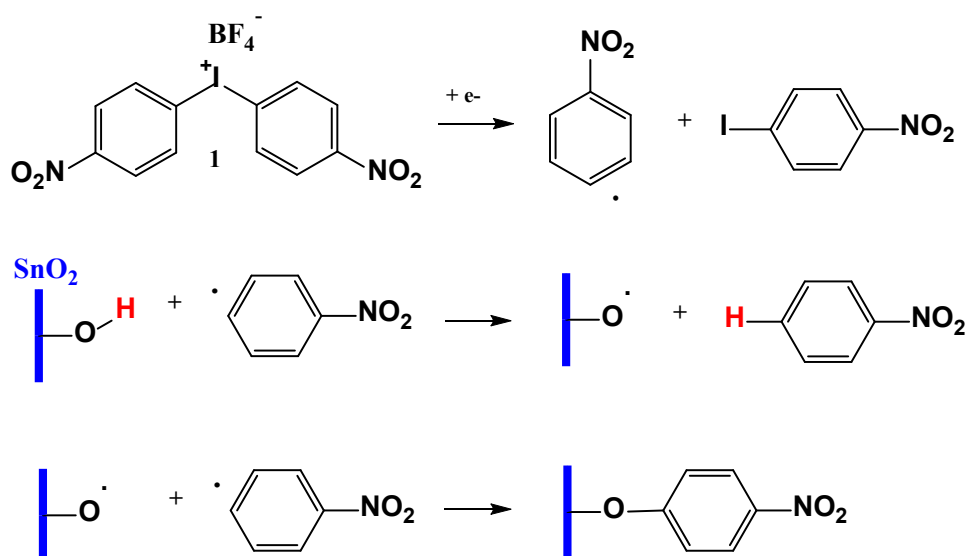
Scheme 1 Proposed mechanism for the grafting of a SnO$_2$-surface by the electrochemical reduction of di (4-nitrophenyl) iodonium tetrafluoroborate ion.

The grafting is initiated by a dissociative electron transfer from the FTO electrode to an diaryliodonium salt such as di (4-nitrophenyl) iodonium tetrafluoroborate. This electron transfer leads to the formation of a 4-nitrobenzene radical, and iodonitrobenzene as a by-product. The 4-nitrobenzene radical is able to abstract an H-atom from one of the hydroxyl groups located on the SnO$_2$-surface. The generated surface-bounded oxygen radicals react with excess of free 4-nitrobenzene radicals under oxygen-carbon bond formation and thereby binding the 4-nitrophenyl group covalently to the SnO$_2$ surface.

In this paper, we report on the electrochemical grafting of FTO electrodes as applied in DSCs by the iodonium and diazonium salts shown in Scheme 2 as well as the analysis of electrode surfaces grafting with the help of Attenuation Reflection Fourier Transform Infrared (ATR-FTIR) and X-ray Photoelectron Spectrocopy (XPS). In addition, cyclic voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were applied to measure the insulation effect of grafting by aid of ferrocene and ferrocyanide as sensitive one-electron probes, respectively [20].

Finally we report results regarding the effect of FTO grafting with di (4-nitrophenyl) iodonium tetrafluoroborate on the performance of DSCs prepared with one of the following dyes: N719, D5 and D35 in combination with either I^-/I_3^- or $[Co(bipy)_3]^{2+}/[Co(bipy)_3]^{3+}$ as redox mediators (Scheme 2).
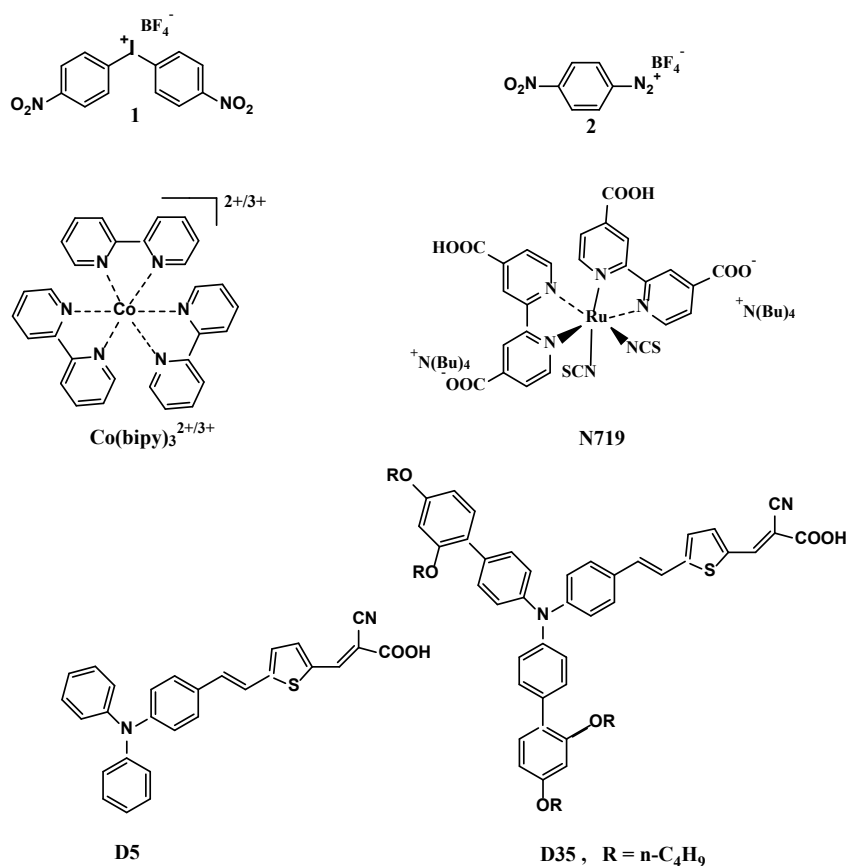
Scheme 2 Overview of investigated iodonium and diazonium salts, dyes and cobalt mediator.

2. Experimental section

2.1. Reagents and materials Di(4-nitrophenyl)iodonium tetrafluoroborate (**1**) was synthesized according to Gerba *et al.* [21]. The synthesis protocol is described in Supporting Information (S1). The starting materials 1-iodo-4-nitrobenzene, 3-chloroperbenzoic acid, boron trifluoride diethyl etherate 4-nitrobenzeneboronic acid were purchased from Sigma Aldrich. Tetrabutylammonium tetraflouroborate (TBABF$_4$) and 4-nitrobenzenediazonium (**2**) was synthesized according Lund *et*

al. [17]. The onium salts **1** and **2** were stored at -18 ℃. The N719 dye was obtained from Solaronix, Aubonne, Switzerland. Iodine (99.8%), 4-*tert*-butylpyridine (4-TBP) (96 %), lithium iodide (99 %), tetrabutylammonium iodide and lithium perchlorate were obtained from Sigma-Aldrich and used as received. 3-Methoxypropionitril (3-MPN) was obtained from Sigma-Aldrich and distilled before use. The dyes D5 and D35 together with the cobalt mediators, tris-(2,2'-bipyridine)cobalt(II) di(hexafluorophosphate) (DN-C01) and tris-(2,2'-bipyridine)cobalt(III) tri(hexafluorophosphate) (DN-C02) were all obtained from Dyenamo, Sweden and used as received.

2.2. Preparation of FTO and FTO|TiO$_2$ electrodes FTO electrodes were cut from conducting glass sheets of 10 x 10 cm (TCO22-7, Solaronix) into an area of approximately 3 x 1.5 cm. The electrodes were then cleaned with methanol and dried at 465 °C for 30 minutes. The lower part of the electrodes were carefully covered by electrical insulation tape (Kapton HN polyimide film, Dupont, thickness 50 μm) except for a circular hole with either d = 0.3 cm or d = 0.6 cm, resulting in an exposed area of 0.07 cm^2 or 0.28 cm^2, respectively. This area is the active part of the electrode, where the grafting takes place. All FTO electrodes were washed in acetonitrile (ACN) and sonicated prior to grafting. Transparent (10 μm layer of 20 nm TiO$_2$ particles) and opaque FTO|TiO$_2$ electrodes (a ≈3 μm scattering layer of 300 nm TiO$_2$ on top of the transparent layer), (Solaronix catalog from 2017, number 74111 and 74101), were covered similarly as the FTO electrodes by electrical insulation tape except for the active TiO$_2$-part (0.36 cm^2) of the electrode.

An FTO electrode covered with a blocking layer of TiO$_2$ was used for comparison with the grafted FTO electrodes. The FTO|TiO$_2$(bl) electrodes were purchased from Solaronix (catalog from 2017, number 75201)

2.3. Electrochemical grafting of FTO electrodes Electrochemical modification of FTO electrodes by cyclic voltammetry were carried out in an acetonitrile solution of either 1 mM or 5 mM of various diaryliodonium and diazonium salts with 0.1 M TBABF$_4$ as the supporting electrolyte. The starting potential of the CV scans was 700 mV more positive than the reduction potential of the given salt, and the turning point of the scan was 200 mV more negative than the reduction potential. The solution in the electrochemical cell was purged with an ACN-saturated nitrogen-flow and stirred for a few minutes prior to each grafting experiment. Each electrode was grafted by five consecutive scans at a scan rate of 20 mV/s, followed by another five consecutive scans at the same scan-rate, and thus only interrupted by stirring and purging with the ACN-saturated nitrogen-flow for a few minutes in between the two scan-cycles. Electrodes were subsequently washed in ACN and sonicated for 20 seconds to remove physically adsorbed onium salts. The electrodes were stored individually at room temperature in the dark.

2.4. Transparent and opaque FTO|TiO$_2$ electrodes were modified similar to the FTO electrodes in a solution of the iodonium salt **1** (1 mM in acetonitrile) with purging and stirring for approximately 30 seconds between each scan. The protecting Kapton tape was removed and the electrodes were thoroughly cleaned in acetonitrile and methanol and dried under a nitrogen flow prior to any adsorption of dye.

2.5. Characterization of electrode grafting by CV Grafting efficiencies of modified electrodes were investigated by cyclic voltammetry with ferrocene as redox probe. For modified and unmodified FTO electrodes cyclic voltammetry was carried out in a solution of ferrocene (0.5 mM) and TBABF$_4$ (0.1M) in ACN, at a scan rate of 100 mV/s. The amount of grafted nitro-groups on the FTO electrode was obtained by a reductive CV scan performed in a solution of 0.1 M TBABF$_4$ in ACN at a scan rate of 50 mV/s, similar to the method used previously by Charlton *et al*. [19].

2.6 Characterization of electrode grafting by EIS Electrochemical impedance spectroscopy (EIS), measurements were carried out in a three-electrode electrochemical cell with a modified FTO electrode as working electrode, a pseudo Ag/Ag^+ (0.1M KCl) as reference, and a platinum counter electrode. Measurements were recorded with a Reference 600 Potentiostat/Galvanostat/ZRA from Gamry Instruments with Gamry Framework and Gamry eChem Analyst software. EIS measurements were carried out in a solution of 5 mM $Fe(CN)_6^{3-/2-}$ and 0.1 M KCl in Milli-Q water at a potential equal to the redox potential of $Fe(CN)_6^{3-/2-}$, with frequencies ranging from $1 \cdot 10^5$ Hz to 0.05 Hz with an AC voltage amplitude of 10 mV.

2.7. Surface characterization by ATR-FTIR and XPS ATR-FTIR, attenuated total reflectance infrared spectroscopy, was obtained by a Perkin Elmer spectrometer 2000 equipped with PIKE MLRacle ATR accessory. $FTO|TiO_2$ electrodes were recorded with 100 scans between 4000-600 nm and FTO electrodes with 1000 scans. XPS data was obtained at the Department of Chemistry at Aarhus University, Denmark using a Kratos Axis Ultra-DLD spectrometer (Kratos Analytical Ltd, Manchester, UK). The data was analyzed using CasaXPS software (Casa Software Ltd. Teignmouth, UK).

2.8. Fabrication of DSCs The DSCs were fabricated with a solar cell kit purchased from Solaronix. Prior to fabrication, the $FTO|TiO_2$ photo-anodes were sintered at 465 °C for 30 minutes and subsequently modified by electrochemical grafting. They were afterwards washed in methanol and then left overnight at room temperature in a dye bath, of either 0.5 mM N719 in methanol, 0.2 mM D5 in methanol, or 0.2 mM D35 in ethanol. Unmodified photo-anodes were left to cool and then transferred directly to a dye bath. Immediately upon removal from the baths the photo-anodes were rinsed in methanol and dried under a nitrogen flow. The dye-adsorbed $FTO|TiO_2$ photo-anodes and the platinum counter electrode were sealed using a Test Cell Gasket from Solaronix at approximately150 °C. The electrolyte (see below) was injected through a drilled hole in the counter

electrode by means of a disposable plastic syringe injection kit from Solaronix. The hole was sealed at 150 ºC with a test cell sealing under a test cell cap, both from Solaronix. Finished test solar cells were stored at room temperature in the dark for at least 24 hours prior to any measurements. The electrolyte for the N719 cells was comprised of 0.1 M lithium iodide, 0.6 M tetrabutylammonium iodide and 0.5 M 4-*tert*-butylpyridine (4-TBP) in 3-MPN with a varying concentration of added iodine, i.e. 0.05 M, 0.075 M and 0.1 M. The electrolyte for the D5 and D35 cells was prepared according to [7] and consisted of 0.2 M $Co(bpy)_3$ $(PF_6)_2$, 0.03 M $Co(bpy)_3$ $(PF_6)_3$, 0.1 M $LiClO_4$ and 0.2 M 4-TBP in 3-MPN, with the modification of using 3-MPN as solvent instead of ACN.

2.9. I-V measurements I-V measurements of fabricated cells were obtained by a Keithley 2450 sourcemeter. For the light source served a home build lamp comprised of 19 LEDs of six different wavelengths from 400nm to 1100 nm and constructed according to the protocol of Novickoeas *et al*. [22] . IV measurements were obtained at 1000 W/m^2 and at 90 W/m^2. Light intensity was reduced by a carbon filter held in front of the cell while measuring.

3. Results and Discussion

3.1. Electrochemical grafting Figure 2 shows a series of grafting voltammograms obtained with an FTO electrode as working electrode in an acetonitrile solution of the iodonium salt **1**. A very distinct reduction peak is visible at -830 mV (vs. Ag wire) for the first scan (black line). As the number of scans increases, the size of the reduction peak decreases, indicating that the electrode surface is covered by an insulating organic layer which inhibits further electron transfer between electrode and iodonoium salt **1**.
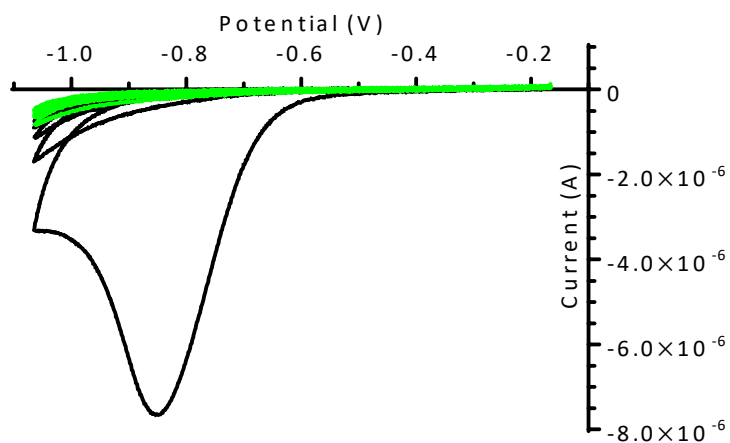
Figure 2 Ten cyclic voltammograms of **1** (5 mM) in ACN on an FTO electrode (0.07 cm^2) at a scan rate of 20 mV/s. The first three scans are depicted black and scans 4-10 are green.

Similarly, FTO electrodes coated with a transparent layer of TiO$_2$ were modified by electrochemical grafting in a solution of **1** (see Figure 3).
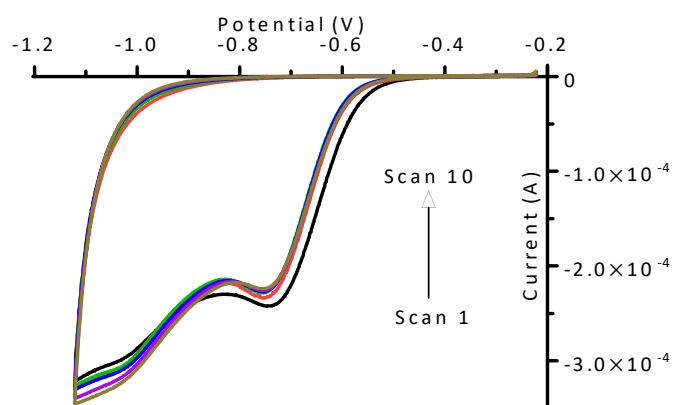
Figure 3 Cyclic voltammogram of **1** (5 mM) in ACN obtained with a Solaronix kit FTO|TiO$_2$ electrode (0.36 cm^2) at a scan rate of 20 mV/s and with stirring and purging with N$_2$ between each scan. Shown are scan 1 (black), 2 (red), 4 (green), 6 (blue), 8 (purple) and 10 (brown). A CV of blank electrolyte is shown in Figure S3.

A reduction peak of **1** is visible in Figure 3 at -740 mV with a reduction current that is approximately 40 times higher than the current peak of the FTO electrode. This may be explained by the much larger surface area of the FTO|TiO$_2$ electrode compared with a bare FTO electrode, and that the TiO$_2$ layer is conducting at the applied negative potential [17]. The reduction peak in Figure 3 shifts to slightly more negative potentials with increased number of scans, indicating that the heterogeneous electron transfer from electrode to the salt is reduced [17]. Similar to grafting of the FTO electrodes, an increase in number of CV scans decreases the reduction current. However, even though the total number of scans in Figure 2 and Figure 3 is the same, the reduction peak current is only slightly reduced with the FTO|TiO$_2$ electrode, whereas the signal of the FTO electrode after 10 scans is essential gone. The FTO|TiO$_2$ electrode contains many more active OH groups on the surface than FTO and therefore more scans are needed in order to graft onto all these additional OH groups as shown in Scheme 1. Approximately 25-30 scans are needed to completely eliminate the reduction peak of **1** at the FTO|TiO$_2$ electrode. After only a few scans, a slight yellow-brownish color could be seen with the naked eye on the active area of the FTO|TiO$_2$ electrodes. The appearance of the yellowish color is likely due to the desired formation of a 4-nitrophenyl-substituted electrode surface. The light transmission of an electrode grafted with 3 CV scans in a solution of **1** (5 mM) is reduced about 15 % at $\lambda = 500$ nm relative to a non-grafted electrode (see Figure S4).

With less than 10 CV scans the FTO|TiO$_2$ electrode is first grafted at the FTO surface followed by coverage of the inner layers of the TiO$_2$ mesoporous structure closest to the FTO electrode. N719 dye absorption experiments on grafted FTO|TiO$_2$ electrode with up to 10 scans in solutions of **1** (1 mM) showed that 83 % of the dye can be absorbed to the electrode relative to the none-grafted

electrode. This indicates that maximum 17% of the OH bonding sites of the TiO_2 surface had been covered by nitro phenyl groups (Table S2).

3.2. Electrochemical characterization The electrical insulation effects of the onium salt grafting of FTO electrodes and of FTO electrodes with a compact blocking layer of TiO_2 were characterized by CV and EIS measurements. Ferrocene and ferrocyanide was used as sensitive redox probes, in the CV and EIS experiments, respectively.

3.2.1. Cyclic voltammetry (CV) measurements obtained with a modified FTO as working electrode and ferrocene as redox probe are shown in Figure 4.
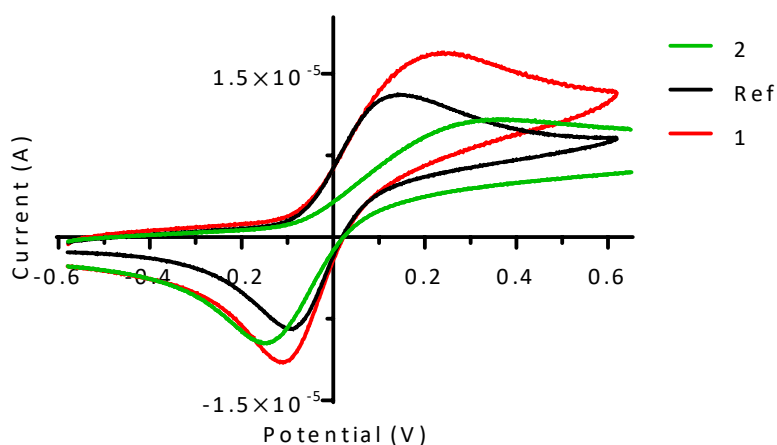
Figure 4 Cyclic voltammograms obtained at 0.1 V/s with modified FTO electrodes (0.07 cm^2) as working electrodes and ferrocene (0.5 mM) as redox probe. With the exception of the reference electrode (Ref = unmodified FTO electrode), all electrodes have been modified in a 5 mM solution of one of the salts **1** and **2** at 2 cycles of 5 scans.

The black curve in Figure 4 is the ferrocene signal from the unmodified FTO-electrode, with a peak separation of 213 mV between the oxidation and reduction peak potentials. Increased peak separation, ΔE_p, is observed for all modified electrodes compared to the unmodified, indicating a

reduction in the electron transfer rate between the electrode and the ferrocene redox probe (See Table 1). Even though grafting with the iodonium salt **1** and the diazonium salt **2** is expected to result in a film of the same chemical species on the FTO-surface, the diazonium salt is allegedly more efficient when it comes to insulating the surface.

3.2.2. Electrochemical impedance spectroscopy (EIS) analysis EIS data of unmodified and FTO electrodes grafted with **1** and **2** together with FTO electrodes with a compact layer of TiO_2 were obtained and analyzed by fitting to the constant phase element, CPE, with a diffusion model (Gamry eChem Analyst). The equivalent circuit diagram of this model is shown in Supplementary (Figure S5). Fitting data to this model yields in the resistance of the solution in the electrochemical cell, the capacitance of the double layer of the interface between electrolyte solution and electrode, and in the charge transfer resistance. The latter one is the resistance that the electron must overcome when moving across the electrolyte/electrode interface. These quantities can be extracted from the Nyquist plot, while the lifetime, τ, of the electron can be extracted from the Bode plot. The lifetime can be calculated from the frequency of the peak generated in the Bode plot, i.e. the frequency f_{min} corresponding to the minimum phase, as in the equation below [17]:

$$\tau = \frac{1}{2\pi f_{min}} \tag{1}$$

The electron lifetime is often referred to as the recombination lifetime and is inversely proportional to the recombination rate (f_{min}), i.e. higher electron lifetimes corresponds to slower recombination rates.

The Nyquist plots and Bode plots of the EIS measurements on electrodes modified with different onium salts, and with different grafting CV scans of **1** are given in Figure 5 and Figure 6 respectively.
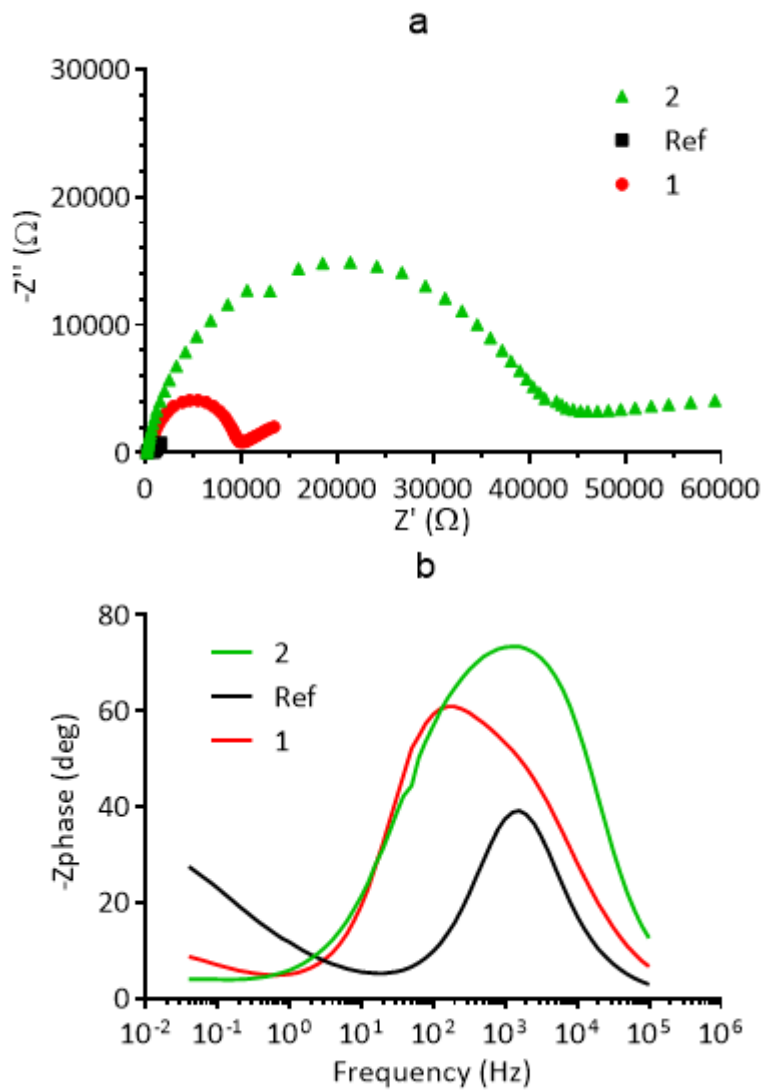
Figure 5 a) Nyquist and b) Bode plots of EIS measurements performed in a 3-electrode set up with a FTO grafted electrode (0.07 cm^2) as cathode, Pt as anode, Ag-wire as reference and a 5 mM solution of Fe(CN)$_6^{4-}$/Fe(CN)$_6^{3-}$ in water. The FTO electrode was grafted with 2 cycles of 5 CV scans in a 5 mM solution of either the salts **1** and **2**.
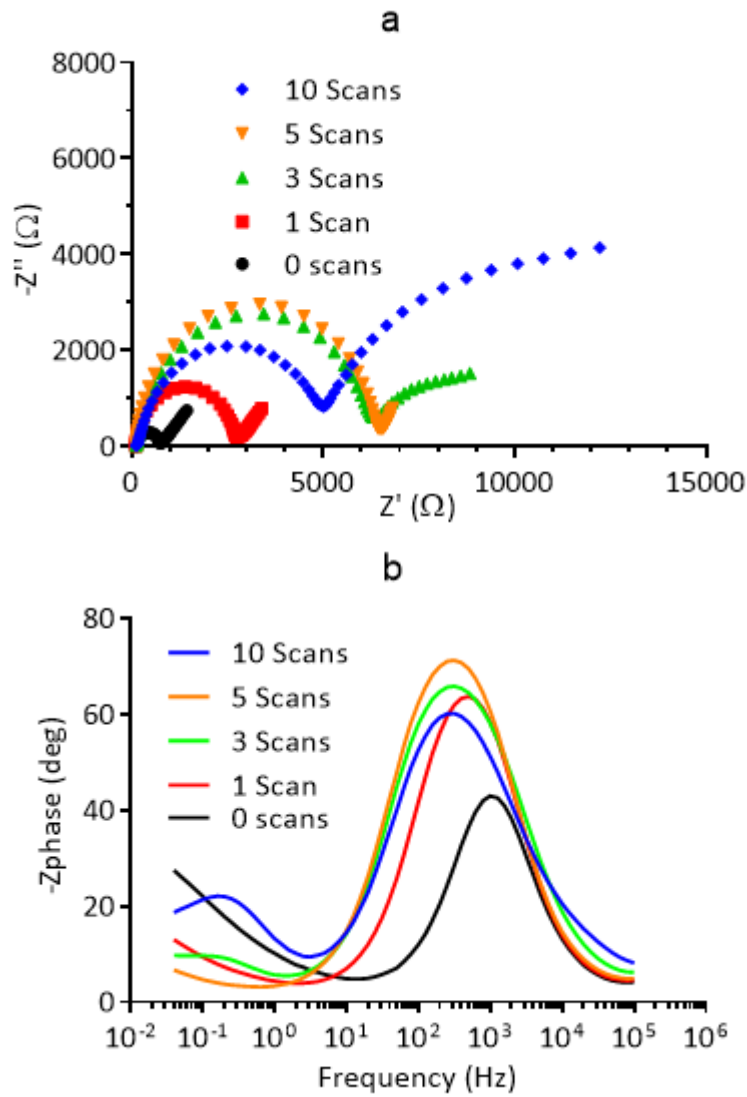
Figure 6 a) Nyquist (a) and Bode plots (b) of EIS measurements of FTO electrodes electrochemically modified by cyclic voltammetry in a solution of **1** (1 mM) at 1, 3, 5 or 10 scans. (Electrode area = 0.07 cm^2).

Table 1 summarize CV peak separations, charge recombination resistance R_{ct} and electron lifetimes of the various electrodes. Table 2 shows the R_{ct} values as a function of CV grafting scans in a 1 mM acetonitrile solution of **1**.

Table 1 CV peak separations of ferrocene and charge transfer resistance R_{ct} of electrochemically surface grafted FTO electrodes[1]

Electrode	ΔE_p/mV	R_{ct} [Ω]	f_{min} [Hz]	τ [ms]
FTO	213	592	1498	0.11
FTO|TiO$_2$(bl)[2]	203	3050	443	0.36
FTO|**1**	296	9862	383	0.42
FTO|**2**	440	41485	790	0.20

[1] FTO electrodes (area 0.07 cm^2) were modified in a 5 mM solution of **1** or **2** in acetonitrile by cyclic voltammetry with 2 cycles of 5 scans. The electrodes were used to obtain CV´s of a ferrocene redox probe (0.5 mM in acetonitrile) with a scan rate of 0.1 V/s and in a three electrode ESI experiments in a solution of 5 mM solution of $Fe(CN)_6^{4-}$/$Fe(CN)_6^{3-}$ in aqueous 0.1 M KCl. The EIS data has been fitted to the *CPE with diffusion* model (Figure S5). τ is the calculated lifetime of the electron, estimated from the frequency corresponding to the minimum phase, f_{min}. Quantities are an average of two measurements on one electrode. [2] FTO electrode with a compact layer of TiO$_2$ nano particles obtained from Solaronix.

Table 2 Charge resistance R_{ct} obtained by EIS of FTO electrodes, electrochemically modified by cyclic voltammetry or constant electrolysis in a solution of 1 mM **1**.

Number of CV scans	R_{ct} / Ω	Electrolysis time/ s	R_{ct} / Ω
0	618	0	618
1	2426	5	1818
3	6255	10	3908
5	5903	15	8899
10	4739	60	20695

Table 1 shows a reasonable correlation between the ferrocene peak separations ΔE with the charge transfer resistance R_{ct}. It´s remarkable that the R_{ct} value of the commercial FTO electrode with a compact blocking layer of TiO_2 is relatively small and 3 times smaller than R_{ct} of FTO|**1**. The most insulating layer on TiO_2 is produced by the diazonium salt grafting with **2**. Table 2 shows that the R_{ct} increases from 1 to 3 CV scans and then decrease. The FTO surface is most likely completely covered by the organic layer after just 3 CV scans.

3.3 Surface characterization The iodonium grafted FTO electrode, FTO|**1**, was characterized by ATR-FTIR (Figure S6), XPS (Figure S7) and CV (Figure S8). All XPS spectra have been

deconvoluted into individual components and XPS results are summarized in Table 3. The same three distinct peaks are visible in both the nitrogen 1s spectrum of FTO|1 and FTO|2 confirming their chemical similarities. However, the intensities of the nitrogen peaks are significantly greater for the FTO|2 than the FTO|1. The peak at 406.2 eV can be assigned to the nitro-group [17, 19, 23], confirming the presence of nitro moieties on the surface of the modified electrodes. The peaks at 400.0–400.1 and 402.4–402.5 are more complicated to assign to a specific functional group. Ceccato e*t al*. [24] attributes the latter to the formation of azo-linked multilayers, proposing that the diazonium cation reacts with the surface bound nitro-phenyl through an electrophilic aromatic substitution during the electrochemical grafting. However, such a mechanism cannot explain why the same peak is visible in the FTO|1 spectrum. Charlton *et al*.[19] concluded – based on a study by Yu *et al*. [23] – that the peak observed at 400 eV along with the peak at 402 eV when grafting with 1 are due to reduced nitro species . They proposed several mechanisms, which could account for the supposed reduction of nitro-groups, emphasizing the reaction with protons from either hydroxy-groups on the electrode surface, from water contamination in the solvent, or reduction during the XPS measurements. Nevertheless, assuming some degree of azo-linking could account for the higher nitrogen intensity for FTO|2 when considering that the carbon intensities are almost the same for FTO|2 and FTO|1.

The XPS analysis of the FTO|1 electrode are summarized in the table below. The results are based on one measurement on a single sample.

Table 3 – Summarization of XPS analysis of the FTO|**1** electrode. Binding energies have been assigned to given elements, peaks have been fitted and integrated and elemental concentrations have been estimated.

	1s Carbon peaks		1s Nitrogen peaks			1s Oxygen peaks	
Binding energy [eV]	285.0	286.6	400.0	402.4	406.2	530.7	532.7
Integrated area	120.83	31.16	9.32	2.90	7.48	1.44	5.79
Concentration of element	67.53 %	17.41 %	5.21 %	1.62 %	4.18 %	0.81 %	3.23 %

From the element concentration an estimated N:C ratio can be calculated as 1:7.7, almost consistent with one nitro-group for each phenyl-group (1:6).

A reductive CV scan of a representative FTO|**1** electrode is shown in Figure S8. Integration of the current over the reduction peak of the nitro-group yields the total transferred charge Q which is related to the surface coverage Γ by $Q = nFA\Gamma$, where F is the Faraday´s constant and $n = 1$ and $A = 0.28cm^2$ [19]. The surface coverage of the electrode was estimated to 9.5×10^{-9} mol/cm^2.

3.4.1. Performance of N719 DSCs Solaronix opaque kit electrodes with a scattering TiO$_2$ layer on top of the active TiO$_2$ layer were grafted with various numbers of CV scans in acetonitrile solutions of the iodonium salt **1** (1mM). The nitro-phenyl grafted electrodes were used as photo anodes in DSCs with N719 as dye and a standard electrolyte with I$_3^-$/I$^-$ as mediator. Table 4 shows the DSC performance parameters as a function of the total number of grafting CV scans.

Table 4 Characteristics of N719-DSCs obtained at 1000 W/m^2 and with grafted photo anodes (grafted by CV in 1 mM solutions of **1)**.

$[I_3^-]^1$	Scans	V_{oc}	J_{sc}	ff	η
mM		mV	mA/cm^2		%
50	0	786	12.46	0.50	4.87
50	1	749	12.04	0.48	4.32
50	3	698	11.86	0.47	3.88
50	4	740	9.62	0.51	3.60
50	5	713	10.40	0.41	2.99
50	3	698	11.86	0.47	3.88
75	3	743	12.24	0.48	4.40
100	3	734	12.32	0.46	4.14

[1] Electrolyte: 0.1 M LiI, 0.6 M tetrabutylammonium iodide, 0.5 M 4-*tert*-butylpyridine in 3-methoxypropionitrile with a varying concentration of added iodine (50, 75 and 100 mM).

From Table 4 it is evident that the nitro-phenyl film coating onto the photo-anode does not enhance the performance of the N719 DSCs. All performance parameters show a tendency to decrease with increasing degree of grafting. Ito *et al*. showed that the addition of a TiO$_2$ compact blocking layer in DSCs with I_3^-/I^- as mediator only increases the open circuit potential by 20–30 mV. [25] The relative modest V_{oc} improvement obtained by Ito *et al*.[25] demonstrates the that the back electron transfer rate from FTO to I_3^- is a relative minor problem due to the slow electrode kinetics of the two electron I_3^-/I^- redox mediator. The potential gain of applying blocking layers with I_3^-/I^- DSCs are therefore anticipated to be low. We observed a decrease of all cell parameters. In contrast to our expectations, the nitro-phenyl moieties decrease the forward current to the FTO to a larger extend

than hindering the back electron transfer from FTO to I_3^-. Some electron injection loss may be due to a decrease in dye coverage especially on TiO_2 particles close to the FTO surface. This will lead to a loss of injected electrons and a lower photocurrent. Moreover, the addition of a nitro-phenyl film on the inner part of the photo-anode could inhibit transfer of electrons from the semiconducting TiO_2 particles to the conducting FTO layer: TiO_2 particles are bonded to the FTO by sintering, allowing for electron transfer through direct bonding. However, part of the electron transfer could hypothetically happen by electron jumping, which would be hindered by a blocking layer of nitro-phenyl moieties.

Hao *et al*. [26] had earlier suggested that an increase in iodine concentration in combination with suppression of recombination events would possibly lead to high performing DSCs. The bottom rows of Table 4 shows the performance parameters' dependency on the concentration of iodine for cells utilizing N719, and equipped with blocking layers of nitro-phenyl moieties.

An optimum in open circuit potential and efficiency is observed for the cell containing electrolyte with 0.075 M I_3^-. This suggests that the overall gain in performance due to increasing the charge exchange rate at the cathode, overcomes the increased recombination due to increase of I_3^- concentration. However, the best performing cell with increased iodine concentration, 0.075 M, does not perform as well as the equivalent cell without blocking layer and standard concentration of iodine, 0.05 M, as evident from the comparison in Table 4. A blocking layer which does not obstruct forward reactions combined with increased iodine concentration could presumably enhance cell performance.

3.4.2. Performance of D5 and D35 Figure 7 shows the IV curves and Table 5 the performance parameters of DSCs prepared with the organic dye D5 and $[Co(bipy)_3]^{2+/3+}$ as mediator and the photo anode surface grafted with zero or three CV scans in an 1 mM acetonitrile solution of **1**.
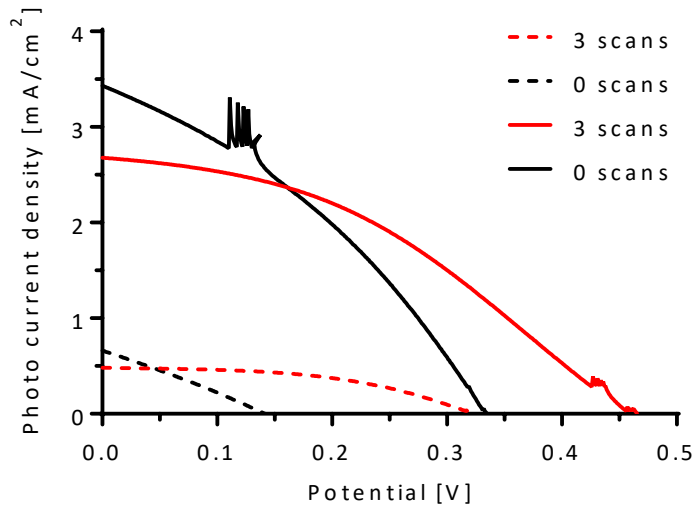
Figure 7 Photocurrent density plotted as a function of applied potential under illumination of 1 sun (full line) and 0.09 sun (dashed line) for D5 based solar cells (0.36 cm^2) with the Co$^{3+/2+}$ mediator. Photo anodes have been electrochemically modified with **1** (1 mM) at 0 or 3 scans.

A significant increase in open circuit potential, fill-factor and efficiency due to application of a nitro-phenyl blocking layer is evident from Figure 7 and Table 5 with only a slight decrease in short circuit photocurrent density. The effect of the blocking layer is especially evident at low light intensities (0.09 sun) where the V_{oc} increase from 141 mV to 323 mV. From the ΔV_{oc} it is possible to calculate the ratio of the back electron transfer from the FTO with ($k_1{}^x$) and without blocking layer ($k_1{}^0$) according to eq. (3). [27]

$$\Delta V_{oc} = 182\ mV = 59\ mV \log\left(\frac{k_1^0}{k_1^X}\right) \Leftrightarrow \frac{k_1^0}{k_1^X} = 10^{182/59} = 1215 \qquad (3)$$

Thus, by application of a grafted blocking layer of nitro-phenyl moieties on the photo-anode the recombination rate can be decreased by a factor of approximately 10^3.

Table 5 Characteristics of the best performing DSCs prepared with D5 or D35 as dye,

$[Co(bipy)_3]$ $^{3+/2+}$ as mediator and photo-anodes surface grafted by **1**.[1]

Dye	CV Scans	Illumination W/m^2	V_{oc} mV	J_{sc} mA/cm^2	ff	η /%
D5	0	1000	333	3.41	0.35	0.39
D5	3	1000	465	2.71	0.38	0.48
D5	0	90	141	0.66	0.27	0.29
D5	3	90	323	0.48	0.48	0.83
D5	Ref[28]	1000	660	11.9	0.68	4-5
D35	0	1000	740	3.65	0.65	1.73
D35	3	1000	660	2.71	0.48	0.85
D35	5	1000	667	2.53	0.49	0.82
D35	0	90	667	1.08	0.64	5.08
D35	3	90	580	0.84	0.47	2.51
D35	5	90	519	0.47	0.44	1.18
D35	Ref[29]	1000	920	10.7	0.68	6.7

[1] Cells have been constructed from modified opaque FTO|TiO$_2$ electrodes (0.36 cm^2) and prepared with a Co$^{3+/2+}$ electrolyte. FTO|TiO$_2$ electrodes were modified by cyclic voltammetry in a solution of 1 mM of **1** at a given number of scans with purging and stirring between each scan.

Even with a nitrophenyl blocking layer, the V_{oc} of the D5-DSCs is substantial lower than the maximum V_{oc} = 1.06 V calculated as the difference between the TiO$_2$ conduction band (-0.5 V vs. NHE) and the cobalt mediator redox potential (+0.56 V vs NHE) [30] . DSCs prepared with the D5 dye and a compact layer of TiO$_2$ on the FTO surface has been reported to have a V_{oc} of 0.66 V [28]. A reason for the relative low V_{oc} for the D5 cells may be caused by the back-electron transfer from the TiO$_2$ surface to Co(bipy)$_3$$^{3+}$. In contrast, bulky dyes like D35 has been shown to reduce the

back electron transfer from TiO_2 [31] and efficiencies of 6.7 % has been obtained of DSCs prepared with D35 and a compact TiO_2 blocking layer [31].

Table 5 shows our results with DSCs fabricated with D35 as dye and the photo anode treated with zero and three CV scans in a acetonitrile solution of **1** similar to the D5 experiments.

From Table 5 it is evident that the application of a film of nitro-phenyl moieties on the photo-anode does not necessarily enhance the performance of a DSC utilizing D35 as dye and $[Co(bipy)_3]^{3+/2+}$ as mediator. In fact, the application of a nitro-phenyl blocking layer significantly decreases the overall cell performance as seen with cells utilizing N719. The efficiency of 1.7% with no blocking layer is quite low which most likely is due to the back-electron transfer from the FTO to the mediator. It is therefore surprising that the grafting of the FTO with nitrophenyl groups does not improve the V_{oc} as shown for the D5-DSCs.

Conclusion

In conclusion, we report on a straightforward electrochemical methodology to cover the FTO layer of the DSC photo anode with an insulating layer of nitro phenyl groups by the reduction of the iodonium salt **1**. The efficiency of the blocking layers were demonstrated by a ferrocene CV test, in which ferrocene CV peak separations increased from 200 to 400 mV, and the charge transfer resistance as measured by EIS increased from 600 to 20.000 Ω depending on the number of grafting CV scans. The EIS analysis showed that the electrochemical grafting with **1** gave a better isolation effect than a FTO electrode with a compact blocking layer on the TiO_2 surface. Surface analysis of FTO and FTO│TiO_2 electrodes by means of XPS and ATR-FTIR methodologies supports the grafting mechanism as proposed in Scheme 1. DSCs prepared with D5 as dye, $[Co(bipy)_3]^{2+/3+}$ as mediator and with FTO│TiO_2 electrodes grafted with 3 CV scans of 4-

nitrophenylidodnium salt **1** showed a V_{oc} increase of 182 mV at 90 W/m^2 corresponding to a reduction in the dark current with a factor of 1000. The D5-DSCs were, however, the only cells which showed improved overall cell performance by the surface grafting with **1**. In contrast, DSCs prepared with N719 and D35 as dyes and photoanodes grafted with **1** showed decreased performance on all cell parameters. At this stage we cannot present a plausible explanation for this observation. Therefore work is in progress in order to identify the underlying problems. This includes in particular the systematic investigation of the DSC performance as a function of the thickness of the isolation layer, and its chemical nature.

References

[1] A. Hagfeldt, G. Boschloo, L.C. Sun, L. Kloo, H. Pettersson, Dye-Sensitized Solar Cells, Chemical Reviews 110(11) (2010) 6595-6663.

[2] M. Gratzel, Recent Advances in Sensitized Mesoscopic Solar Cells, Accounts of Chemical Research 42(11) (2009) 1788-1798.

[3] M. Gratzel, Mesoscopic solar cells for electricity and hydrogen production from sunlight, Chemistry Letters 34(1) (2005) 8-13.

[4] J. Burschka, N. Pellet, S.J. Moon, R. Humphry-Baker, P. Gao, M.K. Nazeeruddin, M. Grätzel, Sequential deposition as a route to high-performance perovskite-sensitized solar cells, Nature 499 (2013) 316-319.

[5] O. Malinkiewicz, A. Yella, Y.H. Lee, G.M. Espallargas, M. Graetzel, M.K. Nazeeruddin, H.J. Bolink, Perovskite solar cells employing organic charge-transport layers, Nature Photonics 8(2) (2014) 128-132.

[6] S.Y. Huang, G. Schlichthörl, A.J. Nozik, M. Grätzel, A.J. Frank, Charge recombination in dye-sensitized nanocrystalline TiO_2 solar cells, Journal of Physical Chemistry B 101(14) (1997) 2576-2582.

[7] S.M. Feldt, G. Wang, G. Boschloo, A. Hagfeldt, Effects of driving forces for recombination and regeneration on the photovoltaic performance of dye-sensitized solar cells using cobalt polypyridine redox couples, Journal of Physical Chemistry C 115 (43) (2011) 21500-21507.

[8] T.W. Hamann, O.K. Farha, J.T. Hupp, Outer-Sphere Redox Couples as Shuttles in Dye-Sensitized Solar Cells. Performance Enhancement Based on Photoelectrode Modification via Atomic Layer Deposition, The Journal of Physical Chemistry C 112(49) (2008) 19756-19764.

[9] S.M. Feldt, U.B. Cappel, E.M.J. Johansson, G. Boschloo, A. Hagfeldt, Characterization of Surface Passivation by Poly(methylsiloxane) for Dye-Sensitized Solar Cells Employing the Ferrocene Redox Couple, The Journal of Physical Chemistry C 114(23) (2010) 10551-10558.

[10] L. Kavan, M. Grätzel, Highly efficient semiconducting TiO_2 photoelectrodes prepared by aerosol pyrolysis, Electrochimica Acta 40(5) (1995) 643-652.

[11] M.S. Wu, C.H. Tsai, J.J. Jow, T.C. Wei, Enhanced performance of dye-sensitized solar cell via surface modification of mesoporous TiO_2 photoanode with electrodeposited thin TiO_2 layer, Electrochimica Acta 56(24) (2011) 8906-8911.

[12] T.W. Hamann, J.W. Ondersma, Dye-sensitized solar cell redox shuttles, Energy and Environmental Science 4(2) (2011) 370-381.

[13] J.-H. Yum, T. Moehl, J. Yoon, A.K. Chandiran, F. Kessler, P. Gratia, M. Grätzel, Toward Higher Photovoltage: Effect of Blocking Layer on Cobalt Bipyridine Pyrazole Complexes as Redox

Shuttle for Dye-Sensitized Solar Cells, The Journal of Physical Chemistry C 118(30) (2014) 16799-16805.

[14] X. Xin, M. Scheiner, M. Ye, Z. Lin, Surface-treated TiO2 nanoparticles for dye-sensitized solar cells with remarkably enhanced performance, Langmuir 27(23) (2011) 14594-14598.

[15] J.H. Park, J.Y. Kim, J.H. Kim, C.J. Choi, H. Kim, Y.E. Sung, K.S. Ahn, Enhanced efficiency of dye-sensitized solar cells through TiCl 4-treated, nanoporous-layer-covered TiO2 nanotube arrays, Journal of Power Sources 196(20) (2011) 8904-8908.

[16] B.A. Gregg, F. Pichot, S. Ferrere, C.L. Fields, Interfacial Recombination Processes in Dye-Sensitized Solar Cells and Methods To Passivate the Interfaces, The Journal of Physical Chemistry B 105(7) (2001) 1422-1429.

[17] T. Lund, P.T. Nguyen, T. Ruhland, Electrochemical grafting of TiO_2-based photo-anodes and its effect in dye-sensitized solar cells, Journal of Electroanalytical Chemistry 758 (2015) 85-92.

[18] K.H. Vase, A.H. Holm, K. Norrman, S.U. Pedersen, K. Daasbjerg, Covalent grafting of glassy carbon electrodes with diaryliodonium salts: New aspects, Langmuir 23(7) (2007) 3786-3793.

[19] M.R. Charlton, K.J. Suhr, B.J. Holliday, K.J. Stevenson, Electrochemical modification of indium tin oxide using di(4-nitrophenyl) iodonium tetrafluoroborate, Langmuir 31(2) (2015) 695-702.

[20] L. Kavan, N. Tétreault, T. Moehl, M. Grätzel, Electrochemical characterization of TiO_2 blocking layers for dye-sensitized solar cells, Journal of Physical Chemistry C 118(30) (2014) 16408-16418.

[21] R.I. Gearba, K.M. Mueller, P.A. Veneman, B.J. Holliday, C.K. Chan, K.J. Stevenson, Atom-scale covalent electrochemical modification of single-layer graphene on SiC substrates by diaryliodonium salts, Journal of Electroanalytical Chemistry 753 (2015) 9-15.

[22] A. Novičkovas, A. Baguckis, A. Vaitkunas, A. Mekys, V. Tamošiunas, Investigation of solar simulator based on high-power light-emitting diodes, Lithuanian Journal of Physics 54(2) (2014) 114-119.

[23] S.S.C. Yu, E.S.Q. Tan, R.T. Jane, A.J. Downard, An Electrochemical and XPS Study of Reduction of Nitrophenyl Films Covalently Grafted to Planar Carbon Surfaces, Langmuir 23(22) (2007) 11074-11082.

[24] M. Ceccato, L.T. Nielsen, J. Iruthayaraj, M. Hinge, S.U. Pedersen, K. Daasbjerg, Nitrophenyl Groups in Diazonium-Generated Multilayered Films: Which are Electrochemically Responsive?, Langmuir 26(13) (2010) 10812-10821.

[25] S. Ito, P. Liska, P. Comte, R.L. Charvet, P. Pechy, U. Bach, L. Schmidt-Mende, S.M. Zakeeruddin, A. Kay, M.K. Nazeeruddin, M. Gratzel, Control of dark current in photoelectrochemical (TiO2/I--I-3(-)) and dye-sensitized solar cells, Chemical Communications (34) (2005) 4351-4353.

[26] F. Hao, H. Lin, J. Zhang, D. Zhuang, Y. Liu, J. Li, Influence of iodine concentration on the photoelectrochemical performance of dye-sensitized solar cells containing non-volatile electrolyte, Electrochimica Acta 55(24) (2010) 7225-7229.

[27] M. Koelsch, S. Cassaignon, C. Ta Thanh Minh, J.F. Guillemoles, J.P. Jolivet, Electrochemical comparative study of titania (anatase, brookite and rutile) nanoparticles synthesized in aqueous medium, Thin Solid Films 451–452 (2004) 86-92.

[28] D.P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt, L. Sun, A novel organic chromophore for dye-sensitized nanostructured solar cells, Chemical Communications (21) (2006) 2245-2247.

[29] X. Jiang, T. Marinado, E. Gabrielsson, D.P. Hagberg, L. Sun, A. Hagfeldt, Structural Modification of Organic Dyes for Efficient Coadsorbent-Free Dye-Sensitized Solar Cells, The Journal of Physical Chemistry C 114(6) (2010) 2799-2805.

[30] M.I. Asghar, K. Miettunen, J. Halme, P. Vahermaa, M. Toivola, K. Aitola, P. Lund, Review of stability for advanced dye solar cells, Energy & Environmental Science 3(4) (2010) 418-426.

[31] S.M. Feldt, E.A. Gibson, E. Gabrielsson, L. Sun, G. Boschloo, A. Hagfeldt, Design of Organic Dyes and Cobalt Polypyridine Redox Mediators for High-Efficiency Dye-Sensitized Solar Cells, Journal of the American Chemical Society 132(46) (2010) 16714-16724.

Supplementary

S1: Synthesis of Dinitrophenyl iodonium tetrafluoroborate **1**

Table S2: Correlation of total number of scans during modification of transparent FTO|TiO$_2$ electrodes with **1** (1 mM) and surface coverage of N719 on given electrodes.

Figure S3: Cyclic Voltammogram of an ungrafted FTO|TiO$_2$ electrode in acetonitrile/0.1 M TBABF$_4$

Figure S4 Transmission spectrum of a Solaronix transparent FTO|TiO$_2$ electrode surface grafted with 3 CV scans in a solution of the iodonium salt **1** (5 mM) relative to an un-grafted electrode.

Figure S5: EIS equivalence diagram used to simulate the EIS experiment

Figure S6: ATR-FTIR spectrum of FTO electrode grafted with **1** (5 mM **)** at 1,3,5, 7 and 10 CV scans with stirring and purging between each scans.

Figure S8:Carbon 1s XPS spectra of a) FTO|**1** and b) FTO|**2**. Both electrodes have been electrochemically modified using cyclic voltammetry in a 5 mM solution at 2 x 5 scans.