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Boosting the efficiency of aqueous solar cells: a photoelectrochemical estimation on the effectiveness of TiCl_4 treatment

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Abstract: Increasing the photocurrent is one of the main objectives of the current research on aqueous photovoltaic cells, the emerging green, alternative technology in solar energy conversion devices. In such a scenario, this work deals with the thorough understanding of the electrochemical and photoelectrochemical effects of the TiCl_4 treatment onto TiO_2 electrodes, a well-known process for traditional dye-sensitized solar cells, and here, to our knowledge, investigated for the first time in water-based systems. From the quantitative evaluation of the photoelectrochemical parameters, it emerges that the TiCl_4 treatment beneficially affects the photovoltaic parameters: it doubles the sunlight conversion efficiency values, inhibits the recombination of photogenerated electrons with oxidized redox mediator ions, and ensures stable and reproducible cell performance at the laboratory scale.

Keywords: Dye-sensitized solar cell; Aqueous electrolyte; TiCl_4 treatment; Recombination; Photocurrent.

1. Introduction

Aqueous electrolytes represent the new frontier of dye-sensitized solar cells (DSSCs), as they guarantee sustainability, safety and durability at the same time [1,2]. After the initial concerns on the possibility of replacing nitrile-based organic solvents by water in the

electrolyte, today the number of publications focused on the development of aqueous DSSCs with reasonably good efficiency values is rapidly increasing [3,4,5]. Noteworthy, these solar cells have recently been integrated with redox flow batteries, which demonstrate their ability to photocharge energy storage devices [6]. Efficiency values close to 6% have already been reported for 100% water-based DSSCs [7] and the current research is focused on the investigation of all the different cell components, including novel sensitizers [5,8], unconventional redox pairs [9,10], stable cathodes [11,12], surface treatments of the photoanode [13,14] and of the redox mediator [15,16].

Treatments of the photoelectrode that leads to the creation of an extra nanolayer of TiO_2 (before and/or after the deposition of the standard layer) are well exploited methods to improve the performance of standard DSSCs [17,18,19]. Post-treatment process can be carried out by TiCl_3 electrodeposition or titanium isopropoxide post-treatment, but the use of titanium tetrachloride (TiCl_4) represents the most successful choice, which leads to the highest increase in the solar cell efficiency [20,21]. Annealing at $450\text{ }^\circ\text{C}$ converts species from the TiCl_4 solution to TiO_2 crystallites onto the TiO_2 nanocrystalline film surface. This results in improved DSSC performance due to the increased active surface area of the electrode films, enhanced dye loading, inhibited charge recombination by barrier effect and, correspondingly, increased light harvesting efficiency. On one hand, the TiCl_4 treatment produces a downward shift in the quasi fermi level (even if other authors proposed an increase of the density of electronic traps corresponding to defective TiO_2 surface sites [20,22]); nonetheless, on the other hand, it does not affect greatly the DSSC potential because it induces a strong reduction of the recombination rate.

In such a scenario, the quantification and proper understanding of the effectiveness of the TiCl_4 treatment on the performance of aqueous DSSCs assembled with TiO_2

photoelectrodes have never been studied, especially in combination with an organic dye. This evaluation is of fundamental importance, also considering the rapid and progressive integration of aqueous DSSCs in hybrid photovoltaic devices. Hence, we propose here a thorough investigation of the procedure (in terms of experimental parameters) for TiCl_4 treatment and its effects on the efficiency and long-term stability of laboratory scale assembled cells, thus finally demonstrating why and in which circumstances the TiCl_4 treatment is able to greatly increase the performance of these emerging aqueous photovoltaic devices. In the current renaissance of DSSCs [23], the present findings pave the way to a wider knowledge of the quantitative effects of the TiCl_4 treatment in different electrolyte environments.

2. Experimental

2.1 Materials

Sodium iodide (NaI), iodine (I_2), titanium tetrachloride (TiCl_4), chenodeoxycholic acid (CDCA), chloroplatinic acid (H_2PtCl_6), ethanol, acetone, *tert*-butanol (*t*-BuOH) and acetonitrile (ACN) were purchased from Sigma-Aldrich. Deionized water (DI- H_2O , 18 $\text{M}\Omega \text{ cm}^{-1}$ at 25 °C) was obtained by Direct-Q 3 UV Water Purification System (Millipore). Sensitizing dye 2-[[4-[4-(2,2-diphenylethenyl)phenyl]-1,2,3,3a,4,8b-hexahydrocyclopento[b]indole-7-yl]methylidene]-cyanoacetic acid (D131) was purchased from Inabata Europe S.A.; the energy levels of the frontier orbitals are -1.26 and 1.04 V vs. NHE for LUMO and HOMO, respectively [24,25]. Fluorine-doped tin oxide (FTO) glass plates (sheet resistance $7 \Omega \text{ sq}^{-1}$, purchased from Solaronix) were cut into $2 \text{ cm} \times 1.5 \text{ cm}$ sheets and used as substrates for the fabrication of both the photoanodes and the counter electrodes [26,27,28].

2.2 Fabrication of the electrodes

FTO-covered glasses were rinsed in mixed acetone/ethanol in an ultrasonic bath for 10 min; solvent traces were removed by flash evaporation at 450 °C on a hotplate. Front electrodes were prepared by depositing a single layer of porous TiO₂ on top of the conductive substrate by means of a manual screen printer with a 43T mesh frame. After deposition of the paste (18NR-T, Dyesol) and 20 min rest to let it bed thoroughly, the TiO₂ layer was dried at 80 °C for 20 min; finally, it was sintered increasing the temperature up to 480 °C in 45 min. The fabricated photoanodes had a thickness of ≈6 μm and active area of 0.25 cm². They were finally reactivated by heating at 450 °C for 20 min and, subsequently, soaked into a D131 dye solution (0.50 mM in *t*-BuOH:ACN 1:1, CDCA was added to the dye solution as coadsorbent as detailed below). Dipping in dye solutions was carried out at 22 °C for 5 h under dark conditions and shaking in a Buchi Syncore platform equipped with a cooling plate [29]. After dye loading, photoanodes were washed in acetone to remove residual dye not specifically adsorbed onto the TiO₂ layer [30,31,32,33,34].

DSSCs fabricated in this work are distinguished in four categories, based on the kind of TiCl₄ treatment performed: i) Untreated (namely, TiCl₄-free); ii) TiCl₄-treated onto the FTO substrate (TiCl₄ on FTO); iii) TiCl₄-treated onto the TiO₂ substrate (TiCl₄ on TiO₂); iv) TiCl₄-treated (twice) onto both the TiO₂ and the FTO surfaces (TiCl₄ on TiO₂+FTO). When treated, substrates were incubated for 30 min into a 40 mM TiCl₄ aqueous solution at 70 °C, then washed in deionized water, dried with nitrogen gas, and heat treated at 450 °C for 30 min [35,36,37,38,39].

As regards the preparation of the counter electrodes, FTO conductive glasses were platinized by spreading a H_2PtCl_6 5.0 mM solution onto the plate surface and heating up to 400 °C by a hot plate.

2.3 Fabrication and characterization of aqueous DSSCs

Photoanodes were faced to the counter electrodes exploiting Surlyn[®] thermoplastic frames (internal area 0.6 cm × 0.6 cm) as spacers (60 μm thick), taking care of the overlapping of the active areas. These components were assembled by hot pressing (20 s) at 110 °C. The electrolyte solution (consisting of NaI and I_2 dissolved in CDCA saturated water) was injected by vacuum backfilling process through a hole in the Surlyn[®] frame, which was then sealed by commercial epoxy glue [40].

In a previous work [41], we identified – by means of a chemometric approach – the two best conditions for photoanode sensitization and electrolyte formulation of additive-free truly 100% aqueous DSSCs. Exploiting the previous expertise in this respect, here we developed the two optimised lab-scale DSSCs, namely System 1 and System 2 in **Table 1**, which were used to investigate the TiCl_4 treatment effects.

Table 1. Photoanode sensitization conditions and electrolyte formulation of aqueous DSSCs studied in this work.

	CDCA:Dye molar ratio	[NaI] (M)	[I ₂] (mM)
System 1	18:1	5.0	10
System 2	50:1	1.0	10

Photovoltaic performances were evaluated recording three consecutive photocurrent density vs. photovoltage curves on a Keithley 2420 Source Measure Unit, keeping a scan rate equal to 20 mV s⁻¹. Cells were irradiated under simulated 1 sun light intensity (100

mW cm⁻², AM 1.5G) after calibration by silicon diode. Electrochemical impedance spectroscopy (EIS) data were obtained by a CH Instruments Inc. Model 680 potentiostat in the frequency range between 100 kHz and 0.1 Hz. The amplitude of the AC signal was 10 mV. Spectra were recorded under dark conditions at applied DC potentials equal to the previously measured V_{oc} values under 1 sun. Open circuit voltage decay (OCVD) measurements were performed using the above mentioned potentiostat; DSSCs were kept under constant illumination at the open-circuit conditions, and then the illumination was interrupted and the voltage decay recorded as a function of time.

3. Results and Discussion

3.1 $TiCl_4$ treatment: effect on photovoltaic parameters

The experimental study on the effects of $TiCl_4$ treatment was carried out on two different types of cells, namely System 1 and System 2, having the higher and lower dye coverage and redox mediator contents, respectively, which were deeply characterised in a previous work [41]. These two cells provided similar PCE values (1.25 and 0.95%, respectively), which were nonetheless obtained by rather different characteristic parameters (see **Table 2**). Indeed, the cell fabricated following System 1 showed higher J_{sc} and lower V_{oc} with respect to its counterpart (System 2), as expected for a DSSC containing high amount of sensitizer molecules on the photoanode and iodine species in the electrolyte. UV-Vis spectra of thin photoanodes are given in **Figure A.1** in **Appendix A**.

The $TiCl_4$ treatment was performed for 30 min onto the FTO substrate, onto the TiO_2 film or on both these layers (in the latter case, the process was repeated twice). Photocurrent density vs. photovoltage curves of the resulting aqueous DSSCs are shown in **Figure 1**, and the corresponding photovoltaic parameters [i.e., short-circuit current

density (J_{sc}), open-circuit potential (V_{oc}), fill factor (FF) and power conversion efficiency (PCE)] are listed in **Table 2**.

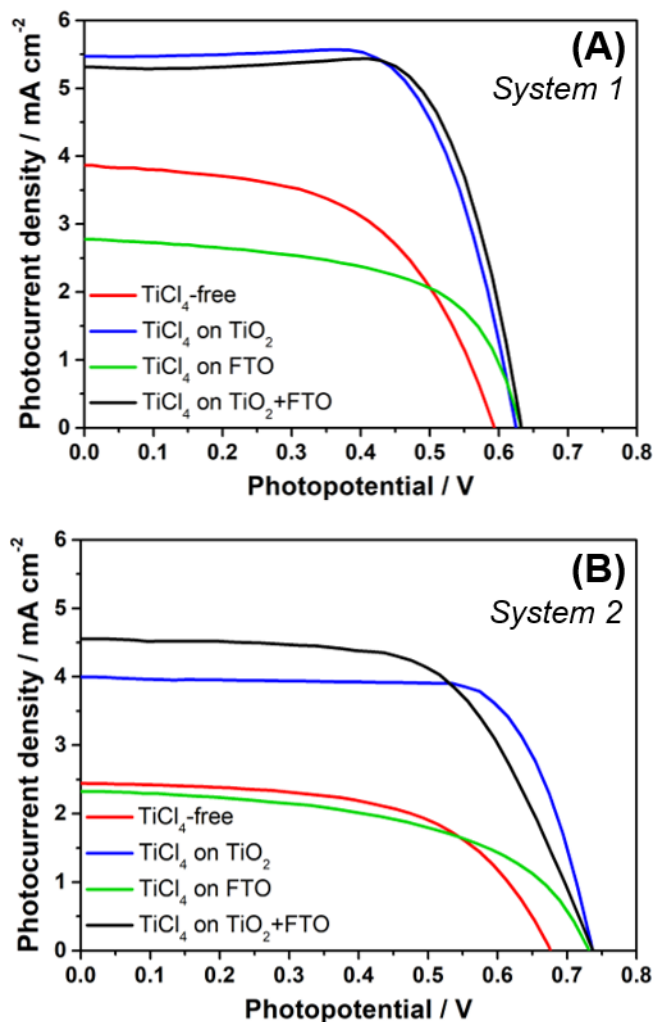


Figure 1. Photocurrent density vs. photovoltage curves (measured under 1 sun irradiation) for aqueous DSSCs with different TiCl₄ treatments. Cells were fabricated according to the protocols developed for System 1 (A) and System 2 (B).

Table 2. Photovoltaic parameters of aqueous DSSCs fabricated following different TiCl₄ treatments. The last column describes the efficiency variation with respect to the pristine (TiCl₄-free) device. Reported values are the best values of a batch of 3 cells; the average of the photovoltaic values is given in brackets.

Cell	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)	Δ PCE
System 1					
TiCl ₄ -free	3.86 [3.81]	0.59 [0.58]	0.55 [0.54]	1.25 [1.19]	–

	TiCl ₄ on TiO ₂	5.46 [5.40]	0.62 [0.61]	0.70 [0.70]	2.37 [2.31]	+90%
	TiCl ₄ on FTO	2.77 [2.73]	0.63 [0.62]	0.59 [0.58]	1.03 [0.98]	-18%
	TiCl ₄ on TiO ₂ +FTO	5.31 [5.26]	0.63 [0.62]	0.73 [0.72]	2.43 [2.35]	+94%
System 2	TiCl ₄ -free	2.44 [2.41]	0.67 [0.67]	0.58 [0.58]	0.95 [0.94]	-
	TiCl ₄ on TiO ₂	4.10 [4.05]	0.73 [0.72]	0.74 [0.73]	2.17 [2.13]	+128%
	TiCl ₄ on FTO	2.33 [2.31]	0.73 [0.72]	0.53 [0.53]	0.91 [0.88]	-4%
	TiCl ₄ on TiO ₂ +FTO	4.56 [4.53]	0.74 [0.73]	0.62 [0.61]	2.10 [2.02]	+121%

The treatment carried out only onto the FTO substrate led to a decreased J_{sc} and increased V_{oc} , which overall accounted for reduced PCE values by 4 and 18% for System 1 and System 2, respectively. This TiCl₄ treatment caused the formation of a nanolayer of TiO₂ onto the FTO substrate, which behaved as a classical blocking layer thus hindering, at least partially, the recombination between the electrons and the oxidized redox couple [42,43]. However, we noticed that this treatment also lowered the J_{sc} values (-28% in the case of System 1, -4% in the case of System 2). To completely understand this effect further experiments are required, which fall out the scope of this paper. Following the literature in the field it is possible to attribute this behaviour to a moderate blocking of the electron flow between the photoanode and the FTO substrate or to a worsening of the interface between the FTO and the mesoporous TiO₂ caused by the additional layer [44].

In a second attempt, the TiCl₄ treatment was carried out only onto the TiO₂ film previously deposited by screen-printing and, subsequently, sintered. Photocurrent density vs. photovoltage curves shown in **Figure 1** markedly highlight the performance improvements with respect to the untreated cells. All of the three photovoltaic parameters

(i.e., J_{sc} , V_{oc} and FF) remarkably increased, leading to PCE values boosted by 90 and 128% (with respect to the pristine samples) for the cells fabricated accordingly to both System 1 and System 2, respectively. Such a result clearly shows that, regardless of the sensitization conditions or the electrolytes formulation, the $TiCl_4$ treatment onto the TiO_2 electrode is fundamental to enhance the performance of aqueous DSSCs.

The downward shift in the quasi-Fermi level and the reduction of the recombination rate described in the seminal researches by O'Regan and coworkers [20,21] are both clearly reflected in the J_{sc} and V_{oc} variations in this work with respect to untreated photoanodes. J_{sc} values registered the most significant increase, likely ascribed to higher electron injection efficiency as a consequence of the enlarged energy gap between the semiconductor conduction band and excited dye.

Based on the downward shift in the quasi-Fermi level mentioned in the previous paragraph, we would have expected lower V_{oc} values, which was not the case in the previous work. On the contrary, we observed a relatively small enhancement of the V_{oc} (within the experimental error) that could be ascribed to both a reduction of the recombination phenomena at the TiO_2 /electrolyte interface and to the presence of CDCA in the sensitization solution.

Even if a thorough experimental/theoretical investigation of the quasi-Fermi level downward shift (in the vacuum scale) is out of the scope of this work, for the sake of the readers it is necessary to highlight that, after the initial seminal studies by Sommeling and O'Regan [20,21], several studies and hypothesis have been proposed in the literature. For example, it is well known that the $TiCl_4$ treatment produces the rutile allotrope of TiO_2 , regardless of annealing temperature, and consisting of rod-shaped particles [45]. Therefore, a rutile/anatase interface is present on $TiCl_4$ -treated photoanodes. Even if some

recent experiments led to a possible attribution of the downshift of conduction band maximum to rutile [46], the true fundamentals behind this interface are far from being clearly understood.

3.2 TiCl_4 treatment: EIS and OCVD analyses

To shed light on the phenomena described above, EIS and OCVD analyses were performed on the aqueous DSSCs. The Nyquist plots of the impedance response of TiCl_4 -treated (on TiO_2) and untreated cells of System 2, measured under dark conditions at the V_{oc} , are shown in **Figure 2A**, while the EIS parameters obtained fitting the experimental points (with the equivalent circuit shown in the inset of **Figure 2A**) are listed in **Table 3**. The first semicircle is related to the charge transfer at the TiO_2 /electrolyte interface, while the second one (at lower frequencies) corresponds to the diffusion of the redox mediator in the electrolyte. Considering that the diameter of the high frequency semicircle indicates the recombination resistance at the photoanode/electrolyte interface (R_{ct}), **Figure 2A** shows that the TiCl_4 treatment performed onto the TiO_2 -based photoanode partially inhibited the recombination processes occurring between I_3^- ions and injected electrons. This is consistent with the higher V_{oc} values measured for TiCl_4 -treated cells and shown in **Table 2**. As a consequence, such reduction in the recombination rate allowed the flux of injected electrons to build up a higher density of charge in the TiO_2 electrode and this effect compensated for the downward shift of the band edge [20]. The above reported EIS spectra were obtained by the polarization of the photoanode at V_{oc} in dark condition. It is worth to mention that such an approach allows to investigate the electrochemical (rather than photoelectrochemical) properties of the different electrode.

Nyquist plots show that the response due to the processes at the counter-electrode/electrolyte interface are convoluted in the central main semicircle. This is typically observed for aqueous DSSCs [8,13,41,47]. A hypothesis related to the presence of only two semicircles could be based on strongly reduced recombination phenomena in aqueous DSSCs, leading to a wide central semicircle superimposed to the one typically observed at high frequency and related to the Pt/electrolyte interface. This is rather close to what proposed in 1998 by Lindquist's group, who wrote that water molecules, being strongly adsorbed onto the TiO₂ surface, coordinated with the surface Ti atoms and blocked the reaction of I₃⁻ with the electrons in the TiO₂ conduction band; as a result, V_{oc} increased proportionally to the amount of water introduced in the cell [48].

In order to investigate the TiCl₄ effect on photopotential values, OCVD experiments were carried out. **Figure 2B** shows that the cells were initially kept under constant illumination and open-circuit conditions, and then the illumination was interrupted and the voltage decay was recorded as a function of time. During this time, the previously photogenerated electrons underwent recombination, thus reducing their population to a dark equilibrium state. In the resulting curve, higher slopes (measured just after light was switched off) indicate faster recombination phenomena. The untreated DSSC showed a higher slope with respect to the TiCl₄-treated counterpart; the fitted experimental points in the very initial moments after light switching-off gave a 38% enhanced recombination rate for the untreated cell.

The OCVD experiment is also an indirect method for measuring the lifetime (τ_n) of injected electrons, accordingly to the equation:

$$\tau_n = -\frac{k_B \cdot T}{e} \cdot \left(\frac{dV_{oc}}{dt} \right)^{-1} \quad \text{Eq. 1}$$

where k_B is the Boltzmann constant, T is temperature, and e is the electron charge [49]. The equation provided τ_n values equal to 279 and 201 ms for treated and untreated DSSCs, respectively, thus confirming the increased lifetime for electrons photoinjected into a TiCl_4 -treated photoanode.

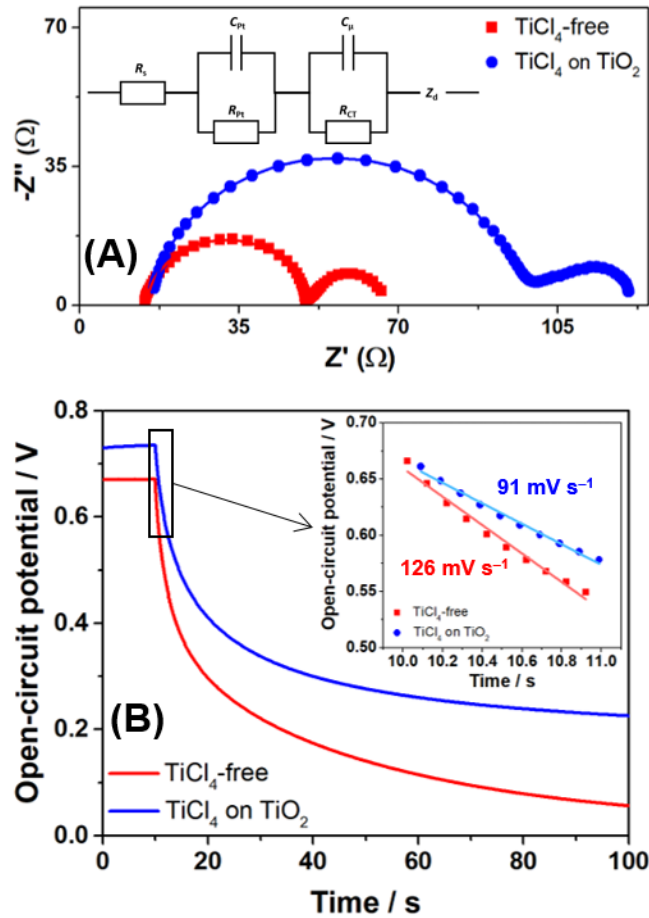


Figure 2. A) Nyquist plots and B) OCVD curves for aqueous DSSCs with and without TiCl_4 treatment. Cells were fabricated accordingly to the protocol developed for System 2.

Table 3. Fitted EIS parameters for aqueous DSSCs with and without TiCl_4 treatment. Cells were fabricated accordingly to the protocol developed for system 2.

Cell	R_s (Ω)	R_{ct} (Ω)	C_{μ} (F)	Z_d (Ω)
TiCl_4 -free	14.7	35.8	1.06×10^{-6}	17.9
TiCl_4 on TiO_2	15.7	82.5	5.12×10^{-6}	23.3

As a further experiment, the TiCl_4 treatment was carried out twice, firstly onto the FTO substrate and then onto the TiO_2 film. Based on the analysis of the photovoltaic parameters listed in **Table 2**, we may exclude a synergistic effect on the PCE values, which resulted indeed very similar to the one obtained for TiCl_4 on TiO_2 only. Therefore, double TiCl_4 treatment does not enhance the PV parameters so markedly to justify its exploitation, particularly from the practical application viewpoint. As a result, in the followings we will just consider TiCl_4 treatment carried out onto the TiO_2 electrode only.

In this work, we also studied the effect of the time of TiCl_4 treatment on aqueous DSSC performances. From the analysis of the experiments carried out in our laboratory, we may confirm that the treatment time (i.e., the duration of electrodes immersion in the TiCl_4 solution) had a relevant effect on the photovoltaic parameters of the resulting aqueous DSSCs. In particular, by increasing the treatment time from 30 to 90 min, an improvement in the current was measured (from 4.19 to 4.60 mA cm^{-2}), in parallel to a faint decrease in potential values (from 0.71 to 0.70 V), the latter being less significant because within the experimental error. Overall, these variations positively affected the PCE values, which increased from 2.01 to 2.29%, corresponding to a +14% improvement. As an example, photocurrent density vs. photovoltage curves for aqueous DSSCs with TiCl_4 -treated TiO_2 electrodes for 30 and 90 min are shown in **Figure 3**.

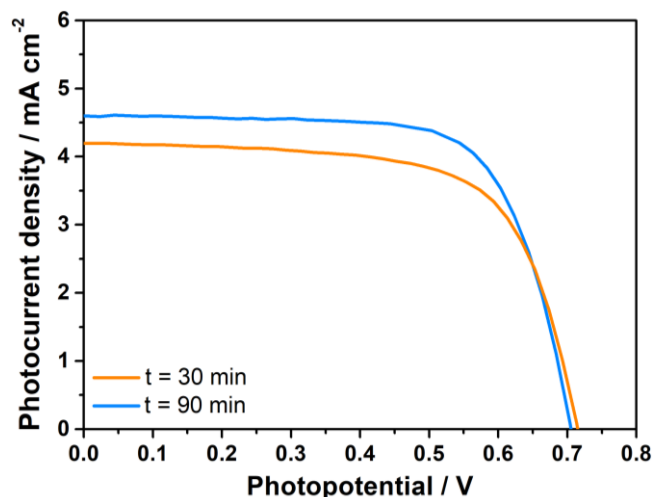


Figure 3. Photocurrent density vs. photovoltage curves (measured under 1 sun irradiation) for aqueous DSSCs assembled with TiO_2 electrodes, which were subjected to different TiCl_4 -treatment (i.e., 30 and 90 min of immersion time in the TiCl_4 solution). Cells were fabricated by the following protocol: CDCA:Dye molar ratio = 50:1, $[\text{NaI}] = 5.0 \text{ M}$, $[\text{I}_2] = 10 \text{ mM}$.

3.3 TiCl_4 treatment: stability issues

The performances of aqueous DSSCs fabricated with TiCl_4 -treated electrodes were measured for 16 days ($\approx 400 \text{ h}$), keeping the cells at ambient temperature under natural indoor light. In details, cells were placed on a laboratory bench exposing the photoanode side towards the ceiling, where neon lamps for ambient irradiation were switched on 12 h per day. Data for untreated cells were already reported in our previous work and were satisfactory [47].

Figure 4 shows the variation of each photovoltaic parameter for two different batches consisting of four cells each, assembled following the protocols of System 1 and System 2, respectively. Overall, both batches of cells were rather stable, thus accounting for the stable performance of the sustainable device components proposed in this study. The photovoltaic parameters values also showed similar variation trends in the two batches: over time, FF values remained almost constant, J_{sc} slightly decreased and V_{oc} progressively increased. The slight V_{oc} increase in the first days was already observed by

other research groups in recent years [50]; it was attributed to a sort of activation of the photoanode after cell assembly. As regards the photocurrent, the cells fabricated accordingly to the protocol of System 2 experienced a more pronounced decrease (−25%) than those of System 1 (−6%). This variation is likely ascribed to the lower amounts of both dye and redox couple contained in the cells assembled following System 2. As a result, little variations that may occur over time (e.g., leakage of electrolyte, degradation of some components upon prolonged cell working, etc.) may significantly impact on the proper operation of the device; on the contrary, in the other batch (System 1) the excess quantity of both dye and redox couple justified the negligible effect on the photocurrent values.

Overall, after 16 days, cells assembled following the protocol of System 2 showed a limited 15% decrease of PCE with respect to the initial value, and cells assembled following the protocol of System 1 underwent a remarkable 8% increase. This is encouraging if we consider that recent literature articles showed lower stability trends for aqueous DSSCs, with more marked decreases compared to our present results: −25% in 200 h (1 sun, [11]), −20% in 2 h (dark, [51]), −37% in 4 h (1 sun, [52]), −50% in 2 h (dark, [53]). The cells we present here, characterized by a light yellow colour and a transparent substrate, would be suitable for indoor applications.

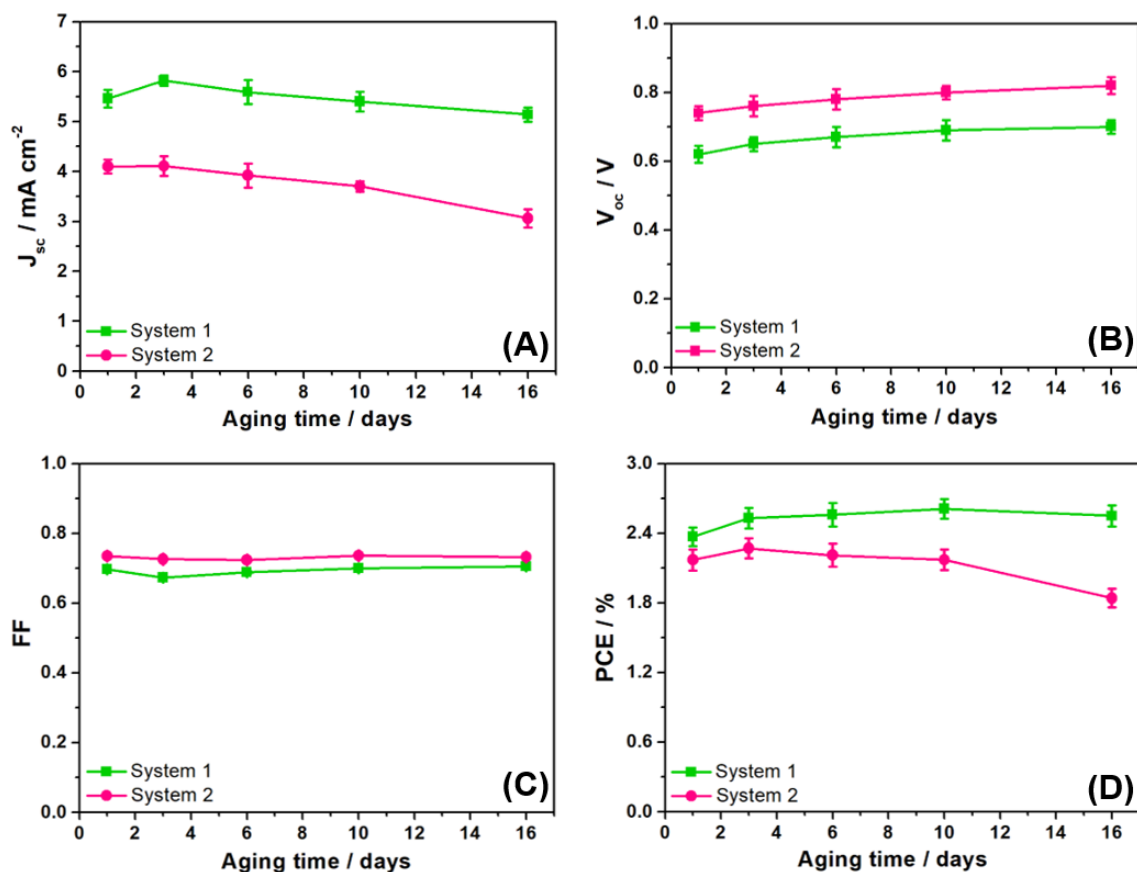


Figure 4. Photovoltaic parameters vs. storage time for aqueous DSSCs kept at ambient temperature under natural indoor light. Each data represents the average of a batch of 4 devices fabricated following the protocols of System 1 and System 2 for the TiCl_4 -treated (on TiO_2) cells.

4. Conclusions

This work demonstrated from a quantitative viewpoint the electrochemical and photoelectrochemical effects of the TiCl_4 treatment carried out on TiO_2 electrodes for aqueous solar cells. Regardless of the sensitization process of the photoanode and the composition of the aqueous electrolyte, the sunlight conversion efficiency increased by over 120% when compared to the untreated solar cell counterparts. The electrochemical and photoelectrochemical investigation showed that both the photocurrent and the potential increased as a result of the TiCl_4 treatment, and the decrease of the

recombination phenomena at the electrode/electrolyte interface is evidenced by an increase of about 40% of the lifetime of photogenerated electrons.

It is worth noting that 100% water-based solar cells can be reproducibly fabricated with efficiencies close to 2.5%, without any additive in the electrolyte nor redox pairs based on heavy metals like cobalt. This work represents a solid benchmark for future studies on these truly sustainable novel photoelectrochemical cells, which are under intense investigation from the scientific community worldwide.

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