

## Solid-state dye-sensitized solar cells made of multilayer nanocrystalline titania and poly(3-hexylthiophene)

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### ABSTRACT

Solid-state dye-sensitized solar cells have been made using nanocrystalline titania, a dye sensitizer and poly(3-hexylthiophene). The main issue in the construction of such cells is ensuring sufficient interface between the oxide and the organic phase. In the present work, improved results were obtained by employing multilayer nanocrystalline titania made of a bottom densely packed layer and a top open structure of varying thickness. The cells were assembled under ambient conditions using silver paste as counter electrode. Thus they were very easy and simple to make. Cells demonstrated a transient behavior characterized by increase in the open-circuit voltage and decrease in the short-circuit current.

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### 1. Introduction

Solid-state dye-sensitized solar cells (SDSC) are made by substituting liquid or gel electrolyte by a hole-conducting (HC) organic material [1–6]. Poly(3-hexylthiophene) (P3HT) [1–3] and 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)9,9'-spirofluorene (spiro-OMeTAD) [4–6] are the most popular choices for this purpose. P3HT has survived, for the time being, all other choices of a conjugated HC polymer, since it is stable [7] and it is endowed with relatively high hole mobility [8]. For this reason, it is also used in the present work. The most important factor that affects SDSC efficiency is “wetting” of the oxide semiconductor [4] by the organic HC material, i.e. sufficient penetration into the oxide mesoporous structure. When the dye sensitizer is excited by absorption of photons, electrons are injected into the conduction band of the semiconductor. The holes left in the dye must be evacuated through the HC material towards the cathode. Of course, the HC material itself, as in the case of P3HT, may absorb light and also act as photosensitizer but experience shows that this role is degraded in the presence of the dye sensitizer [3], as it will be also demonstrated by the present data. What then matters is the direct interaction between dye sensitizer and HC material. Indeed, as it has been previously shown by employing a surfactant dye bearing hydrophobic chains [4], the successful infiltration with the HC material led to a dramatic enhancement of cell efficiency. The role then of the oxide becomes important in the

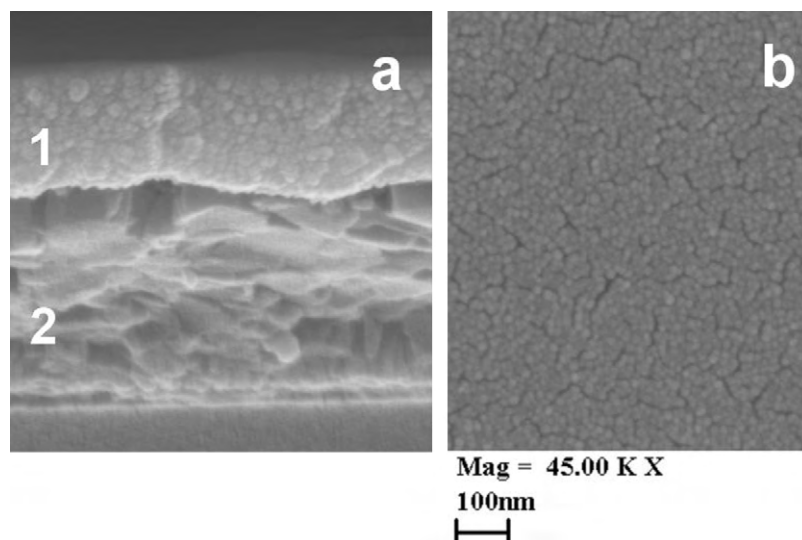
sense that dye distribution and HC material infiltration is dictated by oxide mesoporous structure. Furthermore, the oxide semiconductor remains the material that accepts and transports electrons. Therefore, it must be structured in such a way as to provide large active interface without impeding conductivity. With this in mind, the present work proposes a multilayer deposition of mesoporous titania that leads to enhancement of cell efficiency.

### 2. Experimental

Nanocrystalline titania (nc-TiO<sub>2</sub>) was deposited by sol-gel procedures on transparent conductive FTO glasses (8 Ohm/□, Pilkington, USA). Electrodes were patterned by etching with Zn powder and HCl. The area to be protected was covered with a tape and the area to be etched was exposed. Zn powder was then put on the exposed area covering it. Finally, 37% HCl was injected on the powder with a pipette. The chemical reaction that followed removed all exposed FTO layer. The electrodes were then cleaned, first with soap and then by sonication in ethanol, acetone and isopropanol. A densely packed layer of nc-TiO<sub>2</sub> was first deposited by the following procedure [3]: 1.4 g of the non-ionic surfactant Triton X-100 was mixed with 7.6 ml ethanol. Then we added 1.36 ml glacial acetic acid (AcOH) and 0.72 ml of titaniumtetraisopropoxide (TTIP, Aldrich) under vigorous stirring. This mixture was stable for several weeks if stored in a closed container and it can be used several times. The film was deposited on the FTO electrode by dipping. Only one side (the conductive side) of the electrode was covered with material. The other side was protected by an adhesive tape, which was subsequently removed. The

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**Fig. 1.** FESEM images of the densely packed bottom titania layer: (a) cross-sectional view and (b) top view: (a-1) the nc-TiO<sub>2</sub> layer (~300 nm) and (a-2) the FTO layer (~550 nm). The scale bar (100 nm) corresponds only to (b).

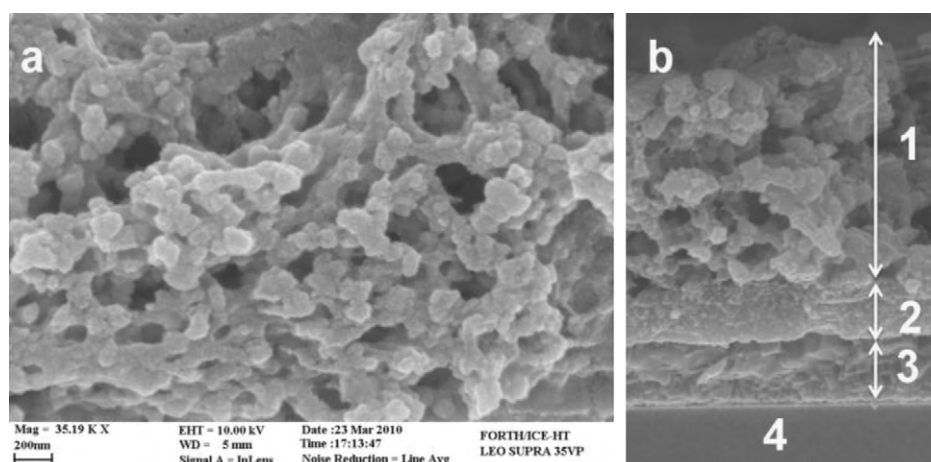
obtained film was dried for a few minutes at 80–100 °C. Then, a second layer was deposited also by dipping. Finally, it was calcined for 10 min at 550 °C with temperature ramped at 20 °C/min. The thus obtained 2-layer film was transparent and had a thickness of about 300 nm, as it will be discussed later. This densely packed film acts both as a blocking layer and facilitates electron transfer. On the top of this film, we deposited several layers of rough nc-TiO<sub>2</sub> by the following procedure: 1 g of polyethylene glycol (PEG, Aldrich) 2000 was dissolved in 8 g of EtOH and then 1 g TTIP was added under vigorous stirring. The electrode bearing the densely structured nc-TiO<sub>2</sub> film was spin-coated with the latter solution at 2000 rpm. It was dried at 80–100 °C and then calcined at 550 °C, as above. This new layer was not transparent, owing to large agglomerates, as it will be discussed later. Its thickness was about 300–350 nm. It could be made thicker by subsequent depositions. This multilayer nc-TiO<sub>2</sub> film was immersed for several hours in an ethanol solution of *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl)-4,4'-dicarboxylato)-ruthenium (II) (Ruthenium 535 or N3, Solaronix) to adsorb dye sensitizer. After rinsing with ethanol and drying at 100 °C, regioregular P3HT (Rieke Metals) was applied by spin coating at 2000 rpm using a 10 mg/ml solution in Chloroform also containing 1 mg/ml lithiumtrifluoromethanesulfonate (Aldrich) and 2 mg/ml 1-methylbenzimidazole (Aldrich). Alternatively, the solvent was substituted by chlorobenzene, lithiumtrifluoromethanesulfonate by Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N (Aldrich) and 1-methylbenzimidazole by *tert*-butylpyridine (Aldrich), introduced at various concentrations [5]. After drying the HC layer at 100 °C, a layer of PEDOT:PSS (H.C. Starck, Baytron P) was applied also by spin coating [3], followed by drying at 150 °C. Finally, silver electrodes were applied by painting [9,10] a viscous silver ink (DuPont 5007E) through a mask. Alternatively, silver electrodes were applied without the intermediate PEDOT:PSS layer. The size of each unit cell was 0.16 cm<sup>2</sup> (2 mm × 8 mm). The silver ink was finally dried for 15 min at 100 °C. The cells were neither sealed nor encapsulated. Their *I*–*V* characteristics were recorded under ambient conditions with a Keithley 2601 source meter while field emission scanning electron microscope (FESEM) images were recorded with a LEO SUPRA 35VP device. Illumination of the samples was made with a PECCELL PEC-L01 Solar Simulator set at 100 mW/cm<sup>2</sup>. The light intensity was measured with a radiant power meter (Oriel-Newport). No calibration of the solar simulator was made other than provided by manufacturer. The radiation was not filtered by any additional filters. Analyses under air-vacuum

were performed using a home-made vacuum chamber and cell holder, evacuated with a rotary pump.

### 3. Results and discussion

The nc-TiO<sub>2</sub> making the anode electrode, as already said, was a multilayer structure. The bottom 2-layer deposition (i.e. two dipping and one calcination steps) was a densely packed [3] smooth film of uniform thickness, as it can be seen by the cross-sectional and top view FESEM image of Fig. 1a and b. TEM and XRD analysis, not shown, revealed that it consists of anatase nanoparticles of around 6–8 nm large [3]. This bottom film plays a double role: it acts as blocking layer preventing short-circuit but also improves electric conduct between the overlying rough film and the FTO electrode. Indeed, as seen in Fig. 1a, a good conduct is achieved between the titania film and FTO layer. On the top of this film we deposited the rough titania film (made in the presence of PEG, as described in the previous section) at varying thickness, by controlling the number of subsequent layers deposition. The FESEM image of that film can be seen in Fig. 2, which reveals a rough open structure. TEM and XRD measurements, not shown, revealed that it also consists of anatase nanoparticles of slightly larger size of 8–10 nm. This rough film allowed substantial dye sensitizer adsorption and deep polymer penetration. It was very hard to image the polymer, at least with the available FESEM tools, but after polymer deposition, it was possible to detect a fine organic layer spreading through the abundant pores of the oxide.

Increase of the thickness of the rough titania film by increasing the number of subsequent layer depositions had a strong effect on cell performance. Table 1 and Fig. 3 show the *I*–*V* data of the cells as a function of the thickness of the top rough nc-TiO<sub>2</sub> film. Most cells were made by introducing a PEDOT:PSS layer between the polymer layer and the silver electrode. All values increased with film thickness. Best performance was observed with cells made of six layers of rough nc-TiO<sub>2</sub>, which, as seen in Fig. 2, had a thickness of 2 μm. Beyond this thickness, the current slightly increased but both voltage and fill factor dropped. The maximum efficiency of 1.36%, demonstrated by the 2 μm cell, is a satisfactory result, if compared with what is usually obtained with such systems [1–3,11–13], taking also into account the fact that the present cells were not optimized but only with respect to the titania film thickness. Further optimization of the cell could be made by affecting several parameters, for example, the chemical nature of the dye sensitizer, the



**Fig. 2.** FESEM images of the rough top layer: (a) top view (scale bar 200 nm) and (b) cross-sectional view: (b-1) the top nc-TiO<sub>2</sub> layer (~2 μm); (b-2) the bottom nc-TiO<sub>2</sub> layer (~300 nm); (b-3) the FTO layer (~550 nm); and (b-4) the glass substrate. The top film is the result of six subsequent layers deposition, each about 300–350 nm thick.

**Table 1**

Photovoltaic characteristics of the cells under simulated 100 mW/cm<sup>2</sup> illumination recorded 4 days after cell assembly, as a function of rough nc-TiO<sub>2</sub> layer thickness.

Thickness of the top rough nc-TiO <sub>2</sub> layer (μm)	<i>J</i> (mA/cm <sup>2</sup> )	<i>V</i> (Volts)	Fill factor	$\eta$
0	0.8	0.40	0.33	0.11
0.35	2.6	0.38	0.36	0.36
0.65	3.0	0.40	0.39	0.38
1.0	3.2	0.39	0.40	0.47
1.3	4.0	0.43	0.41	0.71
2.0	5.5 (4.2) <sup>a</sup>	0.56 (0.68) <sup>a</sup>	0.44 (0.44) <sup>a</sup>	1.36 (1.26) <sup>a</sup>
2.4	5.6	0.50	0.40	1.12
3.0	5.6	0.50	0.37	1.04
2.0 <sup>b</sup>	1.6	0.42	0.35	0.23

<sup>a</sup> Data in parentheses correspond to a cell made without PEDOT:PSS.

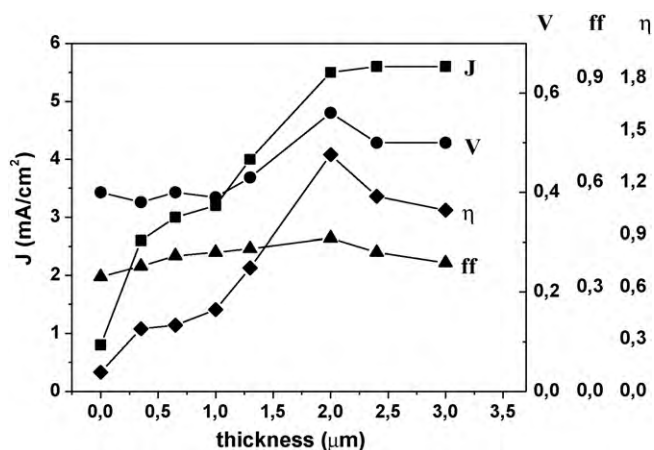
<sup>b</sup> Data obtained in the absence of a dye sensitizer.

concentration of P3HT in the solution used for spin coating, the concentration and the chemical structure of the additives, etc. This has been done by others and it was not the purpose of the present work. The present successful outcome is the result of the open structure of the top titania film that allowed deep polymer penetration. It is interesting to note that by avoiding the PEDOT:PSS layer (see data in parentheses in Table 1), the current was much smaller while the voltage was much larger, leaving the overall efficiency at comparable value. Similar variations were observed with other titania film thicknesses. Obviously, cells made without PEDOT:PSS offer higher

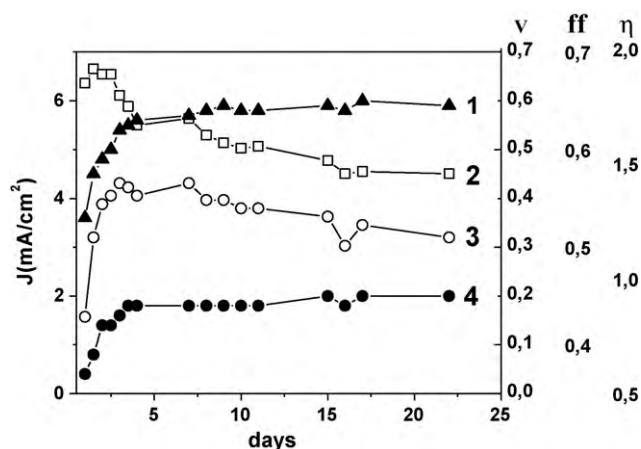
voltage but lower current. The last row of Table 1 demonstrates the importance of the presence of the dye sensitizer. In the absence of a dye sensitizer, the cell did give a photovoltaic response, apparently with polymer acting as a sensitizer but the cell performance was very poor.

The data of Table 1 and Fig. 3 were obtained with chloroform as a solvent for P3HT, and with lithiumtrifluoromethanesulfonate and 1-methylbenzimidazole as additives. When chlorobenzene was used as solvent with Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N and tert-butylpyridine as additives [1,2,4–6], the current dropped by more than 30%. This is contrary to what it is generally believed [8], since most researchers practice the second choice of materials. Even though, these results might not be conclusive, it seems that for the present system the former choice is preferable.

Freshly made cells demonstrated a transient behavior. Open-circuit voltage increased but short-circuit current dropped as can be seen in Figs. 4 and 5. The steepest variation (Fig. 4) lasted about 5 days (cf. Refs. [11,12]). After that period, variation was much slower. The data of Table 1 were recorded on the 4th day. Voltage and fill factor remained practically constant during the remaining period of 25 days but both current and efficiency slowly drifted to lower values. Obviously, the decrease of efficiency is exclusively due to the decrease of the current. One possible reason for this behavior is slow rearrangement of the accommodation of the polymer chains within the pores of titania. Indeed, a faster voltage evolution was observed when the sample was heated up to 200 °C after polymer deposition. Nevertheless, the voltage did increase further, even after this treatment. Use of chlorobenzene as a solvent of P3HT is suggested by many authors [8], mainly because chlorobenzene is less volatile than chloroform, thus it evaporates more slowly during spin coating and permits sufficient time for organic phase

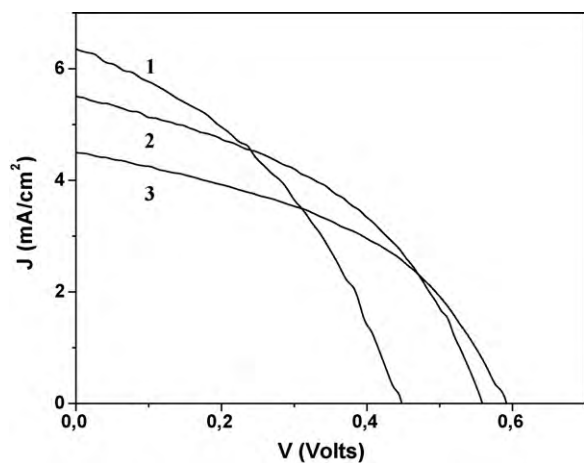


**Fig. 3.** Variation of the short-circuit current density *J*, the open-circuit voltage *V*, the fill factor *ff* and the efficiency  $\eta$  of the cells as a function of the thickness of the top rough nc-TiO<sub>2</sub> film.

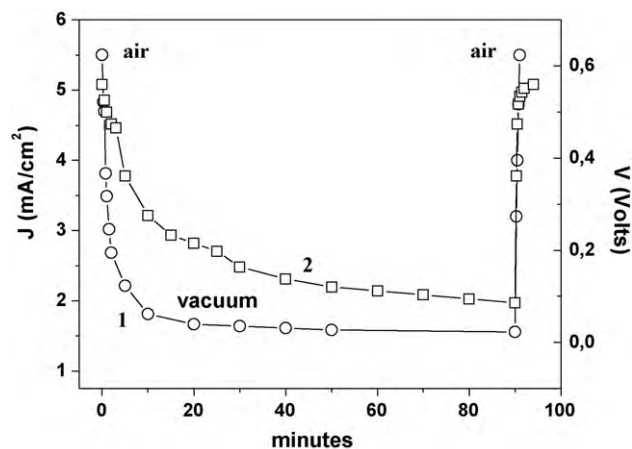


**Fig. 4.** Evolution of the cell characteristics as a function of days passed after cell assembly. The rough titania layer was 2  $\mu\text{m}$  thick (6 layers). Data were recorded at room temperature. The cell was taken out from dark-storing and periodically tested without any kind of pretreatment: (1) open-circuit voltage  $V$ ; (2) short-circuit current density  $J$ ; (3) efficiency  $\eta$ ; and (4) fill factor  $ff$ .

accommodation within the titania mesoporous structure. However, transient behavior was still active no matter what the solvent used was. Apparently, other processes take place, for example, interaction with atmospheric oxygen [3,7,11,12,14]. That oxygen does affect cell performance is seen by the data of Fig. 6 (cf. Refs. [14–16]). Fig. 6 (curve 1) presents the evolution of the current when the cell was placed under vacuum. The short-circuit current was measured in the air, then the air was evacuated and after a steady state was reached the cell was again exposed to the ambient air. It is seen that the current dramatically dropped under vacuum but it recovered in the air. The fact that the cells need air (i.e. oxygen) to function properly was previously observed by other researchers [7,11,12,14–17]. In Refs. [15,16], this phenomenon was demonstrated for several different oxides including  $\text{TiO}_2$  and was assigned to oxygen exchange at the semiconductor surface. Oxygen vacancies in oxide semiconductors may become charge carrier traps but they are quenched in air and the semiconductor properties are thus improved [7]. This has a direct consequence on the measured current. However, not only current but also voltage demonstrates a similar with the current behavior, as seen in Fig. 6 (curve 2). The drop of voltage under vacuum and its increase in the air has been previously assigned to the interaction of oxygen with the polymer. Conjugated poly-



**Fig. 5.** Variation of the  $I$ - $V$  curves during the first 25 days after cell assembly: (1) Day 0; (2) Day 4; and (3) Day 25. These data correspond to the cell with maximum efficiency (2  $\mu\text{m}$  thick rough titania layer).



**Fig. 6.** Evolution of the short-circuit current density (1) and open-circuit voltage (2) when the cell (2  $\mu\text{m}$  thick rough titania layer) was placed under vacuum and when it was exposed back to the ambient air.

mers can form reversible complexes with oxygen [7,12,14,18]. In the case of P3HT, a charge-transfer complex is formed involving the sulfur atom of the thiophene group [7]. This results in an increase of the number of charge carriers [7] and a decrease of charge carrier mobility [18]. Increase of the number of charge carriers leads to higher voltage across the donor-acceptor interface, hence the increase of voltage [12] in the presence of oxygen and its decrease under vacuum. The increase of voltage and the drop of current during exposure in air, i.e. the data of Fig. 4, may then be justified also by this reversible complexation between oxygen and P3HT. Accumulation of charge carriers on the polymer does increase voltage but adversely affects charge mobility. Hence current decreases. Cells like the ones presented in this work do not degrade when stored in the dark, under ambient conditions of temperature and humidity. Therefore, transient behavior is solely due to the above described processes.

The cells of the present work were not exposed to continuous illumination. As already said, the cells were stored in the dark under ambient conditions of temperature and humidity and they were periodically taken out to be tested. In accordance with other researchers, continuous illumination leads to cell deterioration because of photocatalytic degradation of the organic components. Recently, it was shown that improved results can be obtained by doping titania with Nb [19]. These are important issues that there must be always taken into account, even though, they are beyond the scope of the present work.

#### 4. Conclusions

A solid-state dye-sensitized solar cell was constructed using multilayer nanocrystalline titania, a dye sensitizer and poly(3-hexylthiophene) as hole conductor. If we let apart calcination of the titania film, all components were applied under ambient conditions. The metal electrode was painted using a silver ink and can, of course, be applied by printing techniques, like screen-printing. Thus the cell was easy to make. The present work mainly focused on the advantage of using a bottom compact layer of nc- $\text{TiO}_2$  and a top rough layer of nc- $\text{TiO}_2$  at varying thickness, optimized at 2  $\mu\text{m}$ . The top layer provided space for organic phase penetration while the bottom layer assured proper electric conduct. The cells were not sealed but they were stored in the dark and they demonstrated a transient behavior, which was very steep during the first 5 days and much slower later. The main feature of this transient behavior was the increase of voltage and the decrease of current. The cells best performed in the presence of air. On

the contrary, in vacuum both current and voltage dramatically dropped.

The above cells demonstrated a satisfactory performance that could be further optimized. The easiness of fabrication procedure holds promise for future possible large-scale applications. Previous examples of up scaling for similar systems [20,21] may show the way. In this respect, one crucial step for up scaling is finding ways for easy layered titania deposition. This matter is under search in our laboratories.

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