

# Solid State Dye Sensitized Solar Cells using Poly(3-hexylthiophene) as Hole Transport Material

Serap Günes\*, Helmut Neugebauer, Niyazi Serdar Sariciftci

Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University Linz, Linz, Austria

\*Corresponding Author: [serap.guenes@jku.at](mailto:serap.guenes@jku.at), Fax: +43 732 2468 8770.

## Abstract

Solid state dye sensitized solar cells have been fabricated using a ruthenium dye complex, RuL<sub>2</sub>(NCS)/TBA(2:2) (where L= 2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA= tetrabutylammonium), as a sensitizer and poly(3-hexylthiophene) (P3HT) as a hole transporting layer with TiO<sub>2</sub> electrodes as electron transporting layers. We have studied the photovoltaic properties of P3HT/dye coated TiO<sub>2</sub> electrodes and P3HT coated TiO<sub>2</sub> electrodes with and without using compact TiO<sub>2</sub> layers. The compact TiO<sub>2</sub> layer improved the photovoltaic performance of the devices.

## 1. Introduction

Dye sensitized photoelectrochemical solar cells have been subject of intensive research in the last years [1]. Such a cell consists of a nanoporous working electrode formed by a sintered film of TiO<sub>2</sub> semiconductor nanoparticles with a thickness of several micrometers which serves as electron acceptor and transport layer coated with a monolayer of a dye for light absorption and electron injection into the TiO<sub>2</sub> conduction band. An electrolyte solution, either acetonitrile or a mixture of ethylene/propylene carbonate containing the redox couple iodide/triiodide (I<sup>-</sup>/I<sub>3</sub><sup>-</sup>), serves as redox medium to regenerate the photoexcited dye molecules by reduction. Power conversion efficiencies of 10-11 % at AM 1.5 standard solar spectrum (100 mW/cm<sup>2</sup>) have been reported [2-4]. Although these cells show high power conversion efficiencies, their commercial applications is still limited due to stability problems as well as technological aspects of the large module production. The presence of a liquid electrolyte makes the manufacturing process difficult. Therefore, recent efforts in dye sensitized solar cell research are more focusing on replacing the liquid electrolyte with a solid material to eliminate practical problems with sealing. A solid state cell exhibits a structure similar to the dye sensitized photoelectrochemical cells except for the replacement of electrolyte with a p-type semiconductor or organic hole conductor material [5-8]. One of the major differences between dye sensitized solar cells with liquid electrolytes and solid state device lies in the nature of charge transport: in the former case ionic transport is controlled by diffusion whereas in the latter case electronic transport, influenced by conductivity and charge transport mobility, plays an important role [9].

Polymeric materials are of practical interest as replacement for the electrolyte since they are inexpensive and can be tailored chemically to fit a wide range of technological purposes.

Several conducting polymers such as poly (3-octylthiophene) (P3OT), poly (bithiophene) (P3BT), poly (3-methylthiophene) (P3MT), poly (3-hexylthiophene) (P3HT) have already been used in solid state dye sensitized solar cells [10-13].

However, the efficiencies of such solar cells are still lower than that of photoelectrochemical solar cells. Several reasons can be considered for these low efficiencies such as the imperfect filling of the TiO<sub>2</sub> pores by polymeric hole conductor together with the adhesion of the polymer on the TiO<sub>2</sub> or on the dye. Besides that, another important problem is given by charge losses related to back reactions due to a direct contact between the dye regeneration system and the transparent conducting oxide (indium tin oxide (ITO) or fluorine doped tin oxide (SnO<sub>2</sub>:F)). A compact TiO<sub>2</sub> with no pores between the conducting oxide and the nanoporous TiO<sub>2</sub> layer, acting as a blocking layer, has been introduced to prevent these back reactions [14]. Recently, Grätzel and coworkers reported on high efficient solid state dye sensitized solar cells based on spiro compounds [15,16,17,18] employing such compact TiO<sub>2</sub> layers.

In this work, we present the effect of compact TiO<sub>2</sub> layers on polythiophene based solid state dye sensitized solar cells. Such compact layers improve the efficiencies from 0.08 % reported in literature for polythiophene based solid state dye sensitized solar cells to 0.3 %.

## 2. Experimental

ITO was patterned by etching with an acid mixture for approximately 30 min. The part of the substrate which forms the contact was covered with Scotch tape against the etching acid. The Scotch tape was removed after etching and the substrate was then cleaned by using acetone in an ultrasonic bath and finally with iso-propanol.

Dense TiO<sub>2</sub> layers were prepared according to ref [19] and were spincoated under ambient conditions on top of the cleaned and patterned ITO substrates by using 8000 rpm resulting in about 100 nm thick film. The substrates were placed in an oven and sintered at 450 °C for 30 minutes yielding insoluble compact films. A porous TiO<sub>2</sub> layer was deposited by doctorblading commercially available TiO<sub>2</sub> paste on top of the dense TiO<sub>2</sub> films. The substrates were sintered once more at 450 °C for 30 minutes.

The ruthenium dye complex of RuL<sub>2</sub>(NCS)/TBA(2:2) (where L= 2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA= tetrabutylammonium, Solaronix, Switzerland) was used as received. A Ru dye solution was prepared by dissolving 15 mg Ru dye in 50 ml ethanol by using an ultrasonic bath. The TiO<sub>2</sub> electrodes were then immersed into the Ru dye solution for 12 hours.

P3HT with an average molecular weight of 58,000 (American Dye Source) was used as received. 10 mg P3HT was dissolved in 1 ml chlorobenzene. A P3HT film was covered on top of the Ru coated TiO<sub>2</sub> electrodes. Finally, 100 nm gold electrodes were thermally evaporated.

The electrical characterization was carried out under an inert argon environment inside a glove box system (MB 200 from MBraun). For solar cell characterization, a Keithley 236 sourcemeter was used. For the characterization of the devices under AM 1.5 conditions, a

solar simulator (K. H. Steurnagel Lichttechnik GmbH) was. The devices were illuminated through the ITO coated glass.

For measuring the IPCE response between 300 and 900 nm the samples were illuminated under argon atmosphere inside a glovebox with light from a Xenon lamp passing a monochromator (FWHM  $\sim 4$  nm, illumination intensity ranging between  $\sim 50 \mu\text{W cm}^{-2}$  and  $\sim 200 \mu\text{W cm}^{-2}$ ) and chopped with a frequency of 273 Hz. Using an EG&G Instruments 7260 lock-in amplifier the photocurrent of the solar cell was related to the photon flux, determined with a calibrated Si detector

### 3. Results

#### 3.1 Morphology of $\text{TiO}_2$ electrodes

Two kinds of  $\text{TiO}_2$  electrodes were used in this study: (i) dense  $\text{TiO}_2$  electrodes with no pores between the particles (ii) nanoporous  $\text{TiO}_2$  electrodes. The morphologies of both, compact and porous  $\text{TiO}_2$  layers, were characterized by atomic force microscopy (AFM) as shown in figure 1 (a) and (b), respectively. Both types of electrodes were sintered at  $450^\circ\text{C}$  for 30 minutes individually to insure the electrical contact between the particles and also to evaporate the residual solvent remaining between the particles. The AFM images were taken after the sintering procedure. As can be seen from the AFM images the compact  $\text{TiO}_2$  film is rather smooth with a surface roughness of 25 nm whereas the porous  $\text{TiO}_2$  film has a rough surface with a roughness of 100 nm.

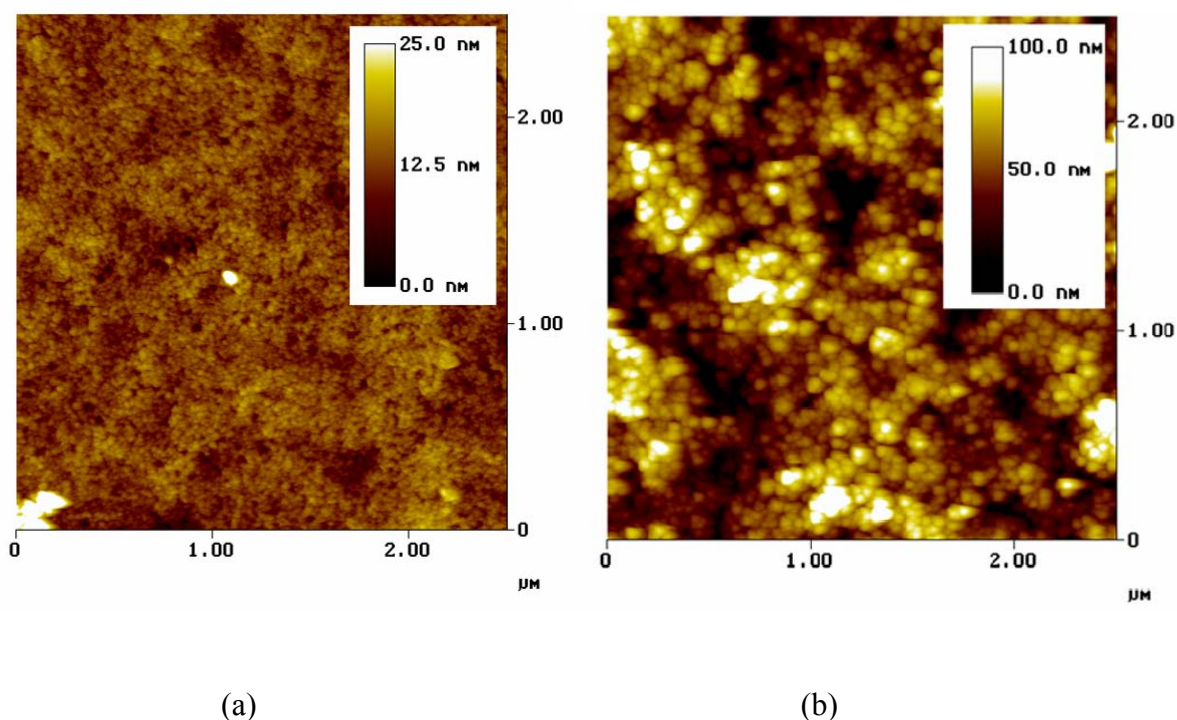
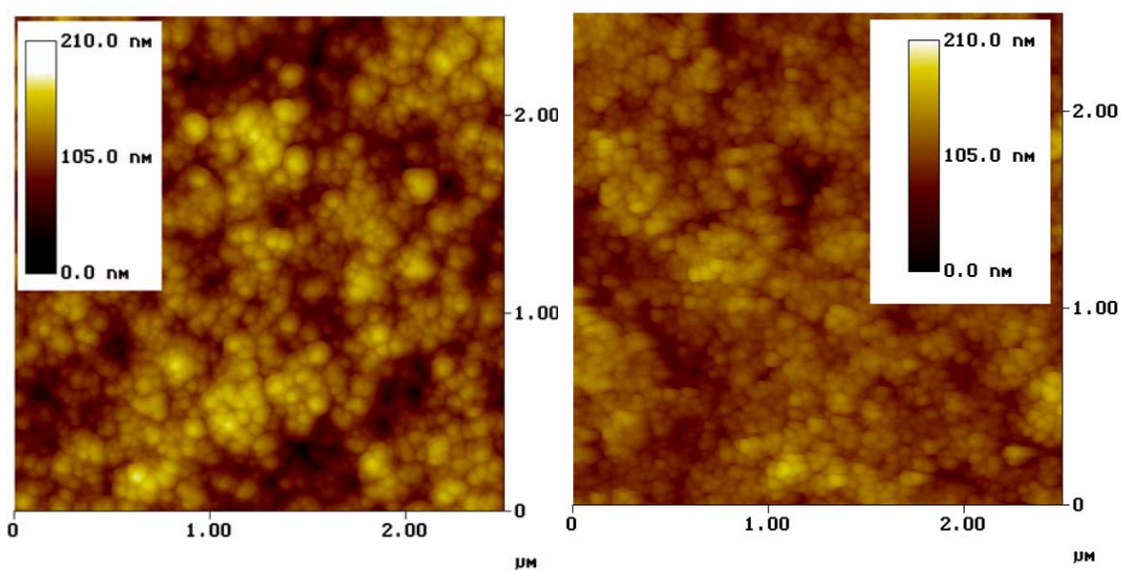


Figure 1. Atomic force microscopy (AFM) images of (a) compact (b) porous  $\text{TiO}_2$  layers.

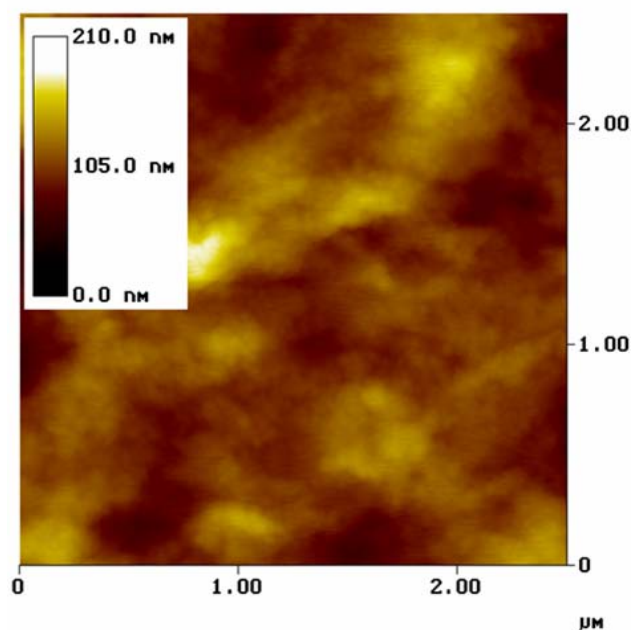
#### 3.2 Effect of P3HT Film Coating Techniques on the Morphology of the Solar Cells

In all solar cell configurations we have chosen gold as a top electrode because its workfunction is close to the highest occupied molecular orbital (HOMO) of the hole conductor P3HT. Thus, hole injection from the polymeric organic material into the metal electrode is energetically possible [8]. However, gold is known to diffuse through the organic materials if the organic layer thickness is not sufficient. Therefore, the film preparation technique of polythiophene layer was optimized. We tried several techniques such as spincoating, doctorblading and dropcasting. Figures 2 (a), (b) and (c) show how these methods affect the morphology. As can be seen, neither by spincoating nor by doctorblading P3HT, the pores of the nanoporous TiO<sub>2</sub> layer are closed, opening pathways for the diffusion of gold causing short circuits in the device. It can be seen from the figure 2 (c) that by dropcasting, the surface of TiO<sub>2</sub> is fully covered with the polymer layer. For the photovoltaic characterization we used the dropcasting technique.



(a)

(b)



( c )

Figure 2. AFM image of a P3HT film prepared by (a) spin casting, (b) doctorblading, (c) dropcasting onto the porous TiO<sub>2</sub>.

### 3.3 Current-Voltage Characteristics

We compared the photovoltaic performance of the solid state devices with or without using compact TiO<sub>2</sub> layers. Figure 3 shows the current voltage (I-V) characteristics of a solid state TiO<sub>2</sub>/P3HT device without using a compact TiO<sub>2</sub> layer in (a) semilogarithmic and in (b) linear scale. This kind of cell produced short circuit current density ( $I_{sc}$ ) of 0.06 mA/cm<sup>2</sup>, an open circuit voltage ( $V_{oc}$ ) of 300 mV and a fill factor of 0.43.

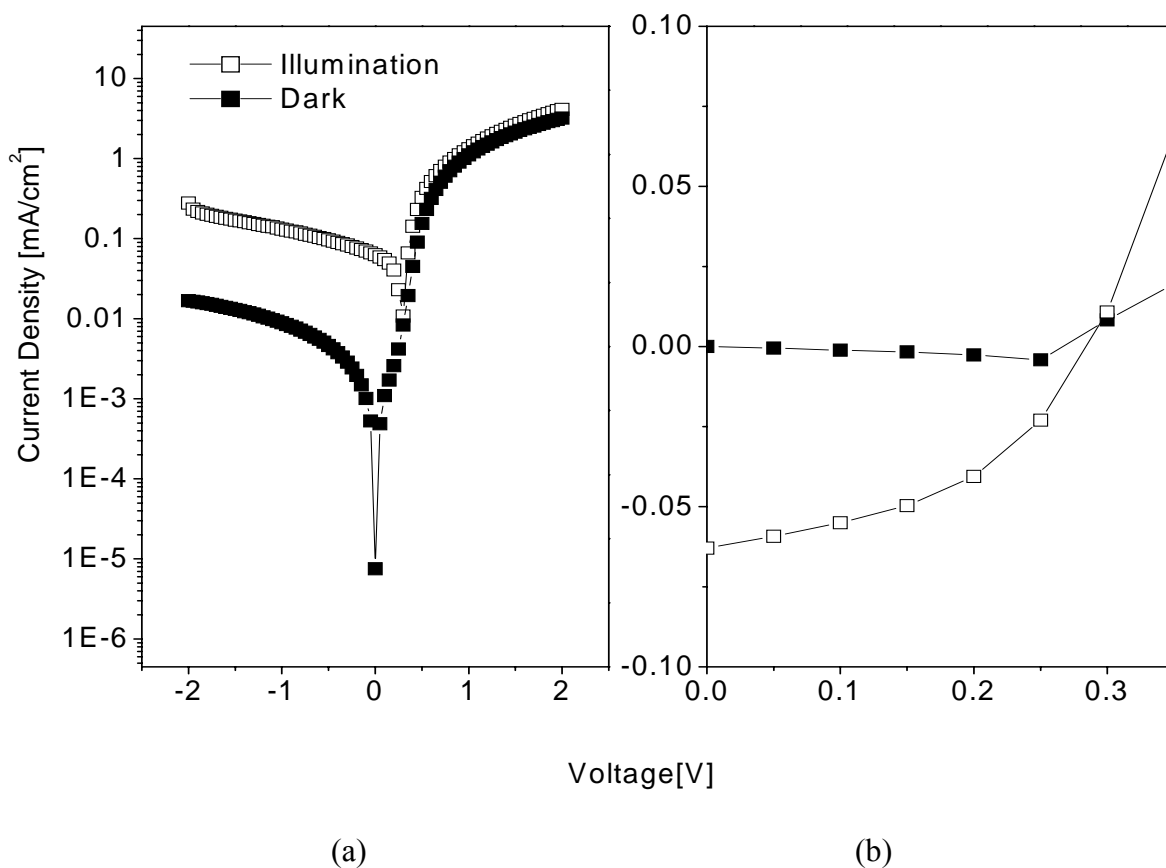


Figure 3. I-V characteristics of TiO<sub>2</sub>/P3HT device without a compact TiO<sub>2</sub> layer (a) semilogarithmic (b) linear scale.

Figure 4 shows the I-V characteristics of a TiO<sub>2</sub>/P3HT device with a compact TiO<sub>2</sub> layer. With the compact layer, the photovoltaic parameters improved to V<sub>oc</sub> of 500 mV, I<sub>sc</sub> of 0.4 mA/cm<sup>2</sup> and a fill factor of 0.5.

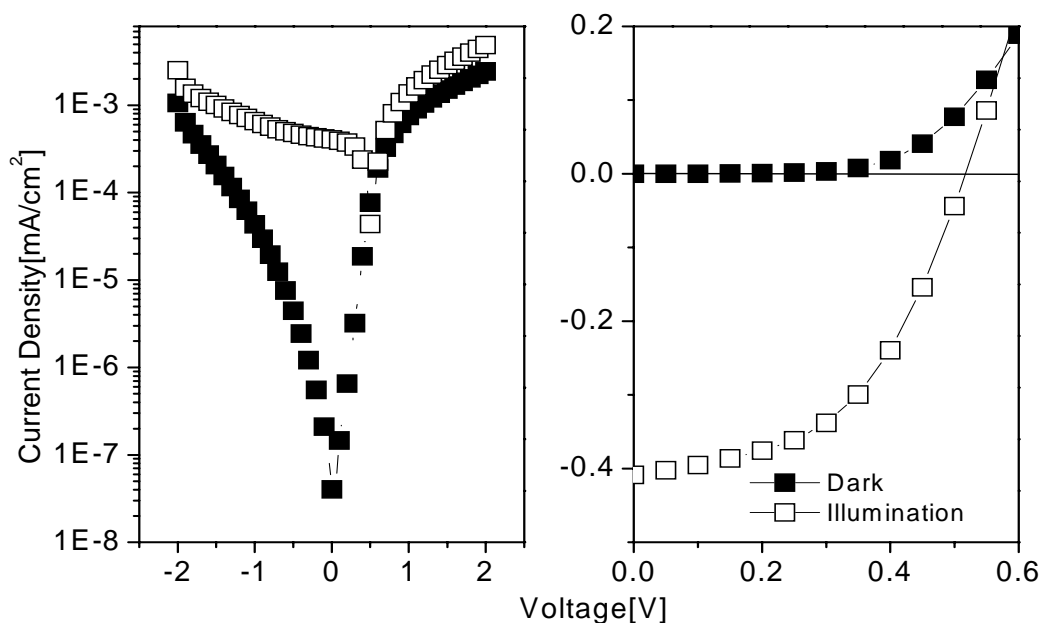


Figure 4. I-V characteristics of  $\text{TiO}_2$  /P3HT device with a compact  $\text{TiO}_2$  layer in (a) semilogarithmic (b) linear scale.

The comparison of the results on the photovoltaic performance with or without compact  $\text{TiO}_2$  layers clearly indicates that the latter improves the short circuit current density by one order of magnitude.

We investigated also the effect of a compact  $\text{TiO}_2$  layer on the dye sensitized solar cells, by introducing a ruthenium dye interlayer between nanoporous  $\text{TiO}_2$  and P3HT. We prepared two kinds of cells (i) with dye but without a compact  $\text{TiO}_2$  layer, (ii) with dye and with a compact  $\text{TiO}_2$  layer. Figure 5 shows the former case. This kind of cell produced an  $I_{sc}$  of  $0.09 \text{ mA/cm}^2$ , a  $V_{oc}$  of  $550 \text{ mV}$  and a fill factor of  $0.3$ .

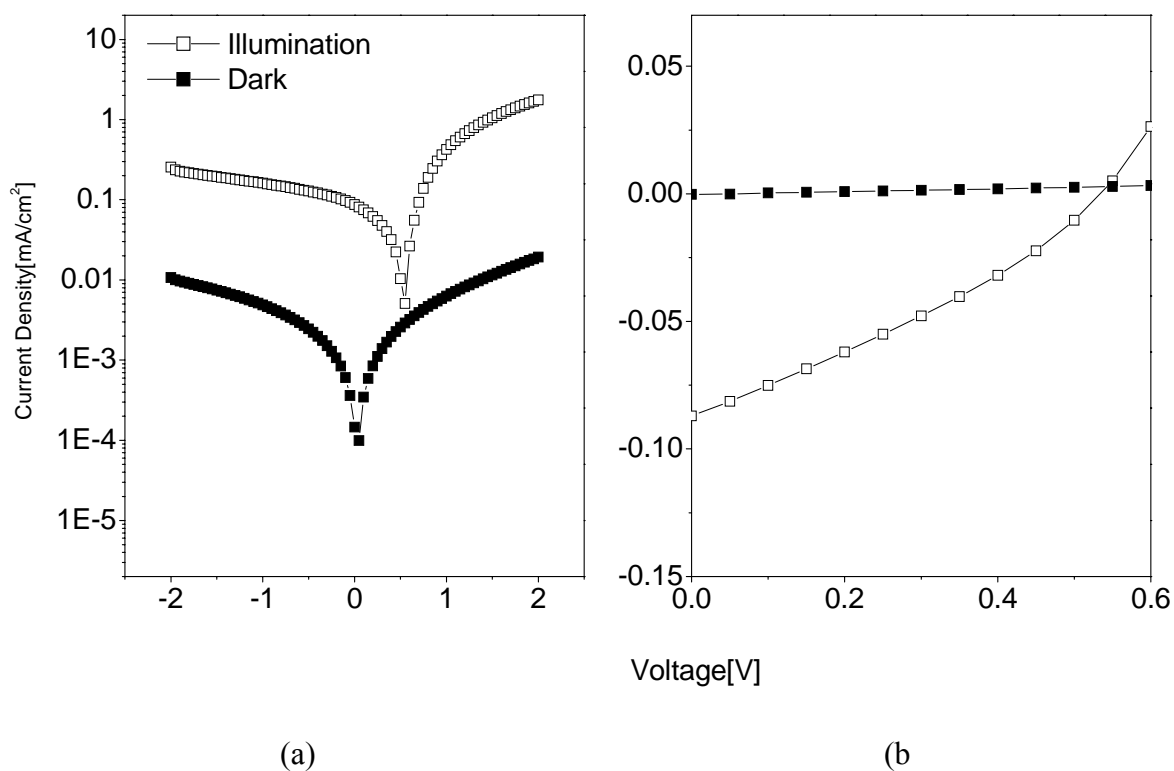
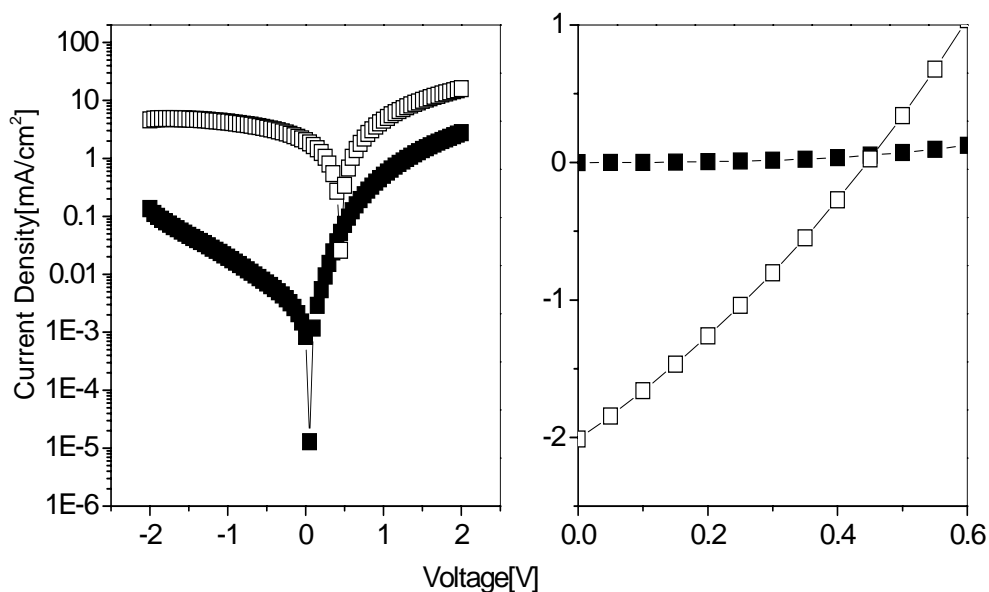


Figure 5. I-V characteristics of a  $\text{TiO}_2/\text{P3HT}$  device with a dye but without a compact  $\text{TiO}_2$  layer in (a) semilogarithmic scale (b) linear scale.

By employing the compact  $\text{TiO}_2$  layer, the properties of the dye sensitized cell are further improved. Figure 6 shows the I-V characteristics of such device, which produced a  $V_{oc}$  of 450 mV,  $I_{sc}$  of 2  $\text{mA}/\text{cm}^2$  and a fill factor of 0.3. Particularly, the improvement of the short circuit current from 0.4  $\text{mA}/\text{cm}^2$  to 2  $\text{mA}/\text{cm}^2$  is remarkable.



(a)

(b)

Figure 6. I-V characteristics of a TiO<sub>2</sub>/P3HT device with a dye interlayer and with a compact TiO<sub>2</sub> layer in (a) semilogarithmic (b) linear scale.

### 3.4 Incident Photon To Current Efficiency (IPCE)

The comparison of the optical absorption spectra of the solar cell components with the IPCE is shown in figure 7. The cells without a compact TiO<sub>2</sub> layer had an IPCE response below 0.1 % (not shown). The cells with compact TiO<sub>2</sub> layers, but without dye, showed IPCE responses around 1.6 % at 550 nm. The IPCE response increased up to 8 % at 550 nm upon insertion of a dye layer between nanoporous TiO<sub>2</sub> and P3HT. This enhancement in the IPCE is mainly attributed to the additional absorption offered by the ruthenium dye.

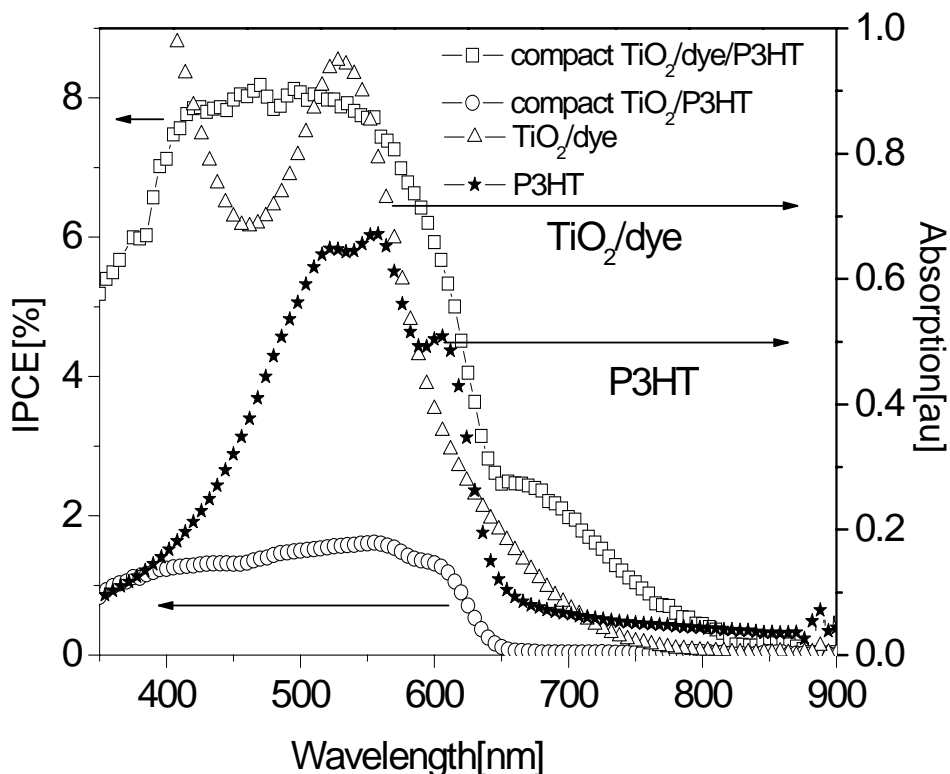


Figure 7. IPCE of  $\text{TiO}_2/\text{dye}/\text{P3HT}$  and  $\text{TiO}_2/\text{P3HT}$  devices with a compact  $\text{TiO}_2$  layer (left y axis), and absorption spectra of  $\text{TiO}_2/\text{dye}$  and P3HT (right y axis).

#### 4. Conclusions

We realized hybrid solid state devices fabricated from compact  $\text{TiO}_2$  and nanoporous  $\text{TiO}_2$  electrodes as electron transporting material and P3HT as organic hole transport material. We investigated the influence of compact  $\text{TiO}_2$  layers on the photovoltaic performance of these solid state hybrid solar cells. The compact layer between the transparent ITO electrode and the nanocrystalline  $\text{TiO}_2$  layer increased the current from  $0.09 \text{ mA}/\text{cm}^2$  to  $0.4 \text{ mA}/\text{cm}^2$ . Further improvement in current was achieved by inserting a dye interlayer between nanoporous  $\text{TiO}_2$  and P3HT. In this case, the current increased up to  $2 \text{ mA}/\text{cm}^2$  yielding an efficiency of 0.3 %. The values are significantly higher than values reported in the literature [8-13] on solid state devices using polythiophenes.

## References

1. B. O'Reagan, M. Grätzel, *Nature*, **353**, 737, (2005).
2. M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphrybaker, E. Muller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, **335**, 6382, (1993).
3. C.J. Barbe, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, M. Grätzel, *J. Am. Chem. Soc.*, **80**, 3157, (1997).
4. M. A. Green, K. Emery, K. Bücher, D. L. King, S. Igari, *Prog. Photovolt. Res. Appl.*, **6**, 35, (1998).
5. A.F. Nogueira, C. Longo and M.A. De Paoli, *Coord. Chem. Rev.* **248**, 1455, (2004).
6. A. Fujishima and X.T. Zhang, *Proc. Jap. Acad. B*, **2**, 33, (2005).
7. B. Li, L. Wang, B. Kang, P. Wang, Y. Qiu, *Sol. En. Mat. Sol. Cells*, **90**, 549, (2006).
8. D. Gebeyehu, C. Brabec, N. S. Sariciftci, D. Vangeneugden, R. Kiebooms, D. Vanderzande, F. Kienberger and H. Schindler, *Synth. Met.*, **125**, 279, (2002).
9. B. Peng, G. Jungmann, C. Jäger, D. Haarer, H.W. Schmidt, M. Thelakkat, *Coord. Chem. Rev.*, **248**, 1479, (2004).
10. G. Smestad, S. Spiekermann, J. Kowalik, C. D. Grant, A. M. Schwartzberg, J. Zhang, L. M. Tolbert and E. Moons, *Sol. En. Mat. and Sol. Cells*, **76**, 85, (2003).
11. L. Sicot, C. Fiorini, A. Lorin, J.M. Nunzi, P. Raimond and C. Sentein, *Synth. Met.*, **102**, 991, (1999).
12. D. Gebeyehu, C.J. Brabec and N.S. Sariciftci, *Thin Solid Films*, **403**, 271, (2002).
13. C. Zafer, C. Karapire, S. Icli, *Sol. En. Mat. Sol. Cells*, **88**, 11, (2005).
14. U. Bach, PhD Thesis, EPFL, Lausanne.
15. U. Bach, D. Lupo, P. Comte, J.E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer, M. Grätzel, *Nature*, **395**, 583, (1995).
16. J. Krüger, R. Plass, L. Cevey, M. Piccirelli, M. Grätzel and U. Bach, *Appl. Phys. Lett.*, **79**, 2085, (2001).
17. J. Krüger, R. Plass, M. Grätzel, H. J. Matthiek, *App. Phys. Lett.*, **81**, 367, (2002).
18. L. Schmidt Mende and M. Grätzel, *Thin Solid Films*, **500**, 296, (2006)
19. L. Kavan and M. Graetzel, *Elect. Chimi. Acta*, **40**, 643, (1995).