

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

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Abstract

Solid state dye sensitized solar cells have been fabricated using a ruthenium dye complex, $\text{RuL}_2(\text{NCS})/\text{TBA}(2:2)$ (where $\text{L} = 2,2'$ -bipyridyl-4,4'-dicarboxylic acid; $\text{TBA} =$ tetrabutylammonium), as a sensitizer and poly(3-hexylthiophene) (P3HT) as a hole transporting layer with TiO_2 electrodes as electron transporting layers. We have studied the photovoltaic properties of P3HT/dye coated TiO_2 electrodes and P3HT coated TiO_2 electrodes with and without using compact TiO_2 layers. The compact TiO_2 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_2 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_2 conduction band. An electrolyte solution, either acetonitrile or a mixture of ethylene/propylene carbonate containing the redox couple iodide/triiodide (I^-/I_3^-), 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^2) 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 TiO₂ pores by polymeric hole conductor together with the adhesion of the polymer on the TiO₂ 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 (SnO₂:F)). A compact TiO₂ with no pores between the conducting oxide and the nanoporous TiO₂ 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 TiO₂ layers.

In this work, we present the effect of compact TiO₂ 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 TiO₂ 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 TiO₂ layer was deposited by doctorblading commercially available TiO₂ paste on top of the dense TiO₂ films. The substrates were sintered once more at 450 °C for 30 minutes.

The ruthenium dye complex of RuL₂(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 TiO₂ 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 TiO₂ 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 ~ 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 TiO_2 electrodes

Two kinds of TiO_2 electrodes were used in this study: (i) dense TiO_2 electrodes with no pores between the particles (ii) nanoporous TiO_2 electrodes. The morphologies of both, compact and porous 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°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 TiO_2 film is rather smooth with a surface roughness of 25 nm whereas the porous TiO_2 film has a rough surface with a roughness of 100 nm.

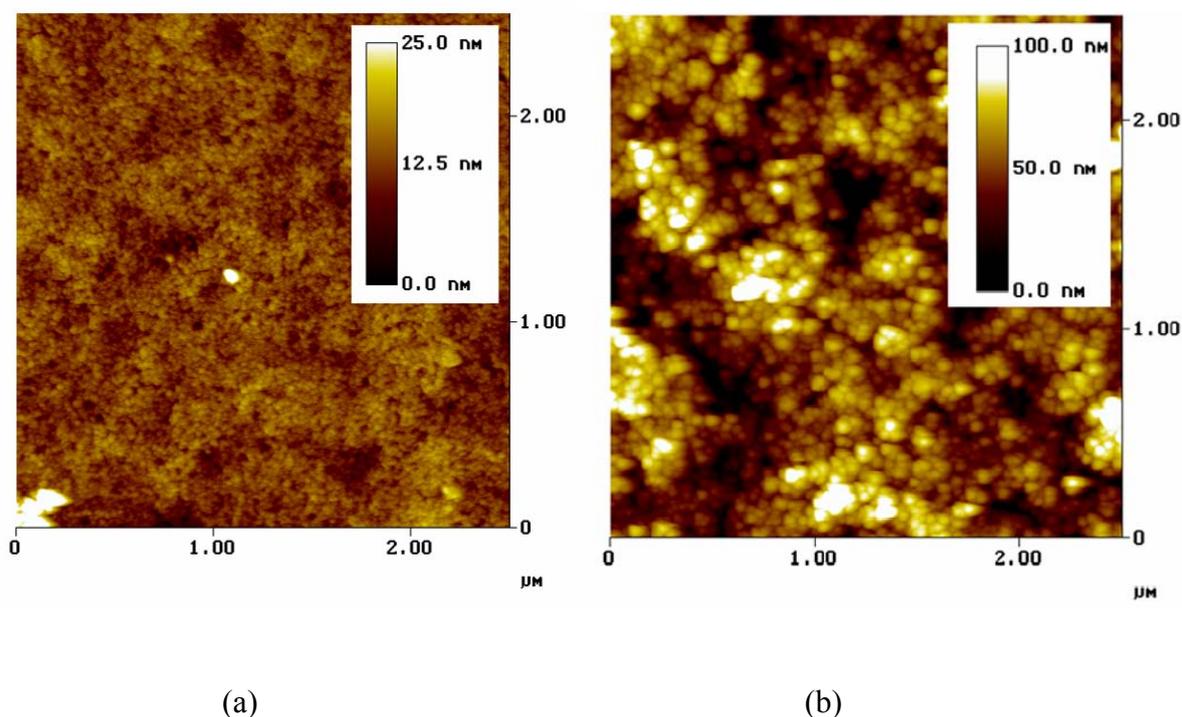
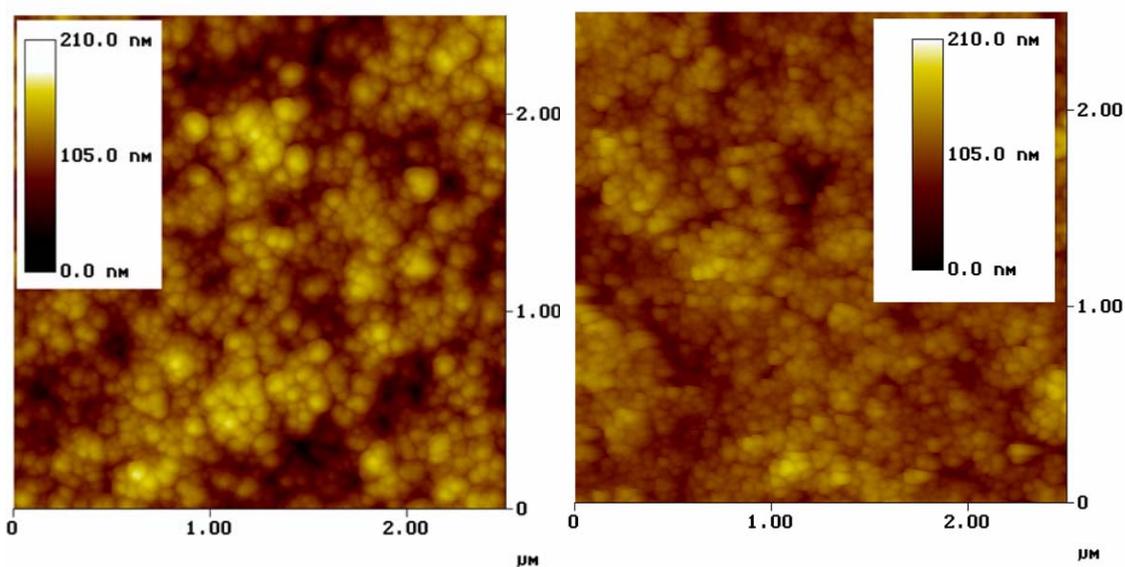


Figure 1. Atomic force microscopy (AFM) images of (a) compact (b) porous TiO_2 layers.

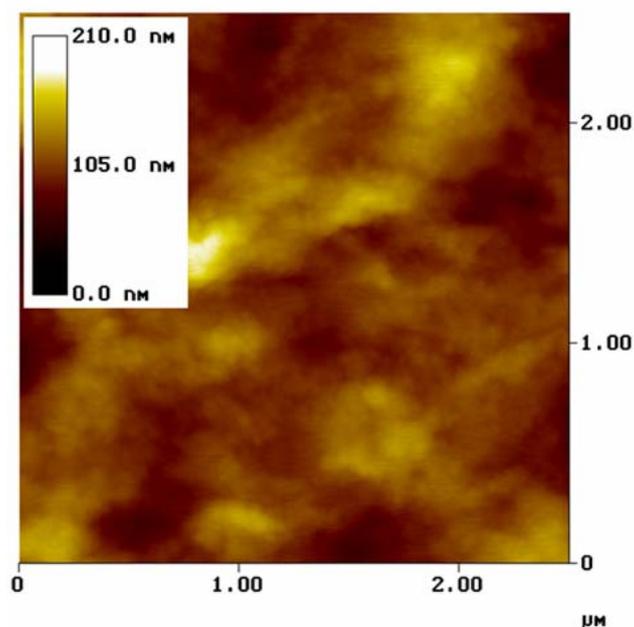
3.2 Effect of P3HT Film Coating Techniques on the Morphology of the Solar Cells

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 TiO₂ 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 TiO₂ 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 TiO₂.

3.3 Current-Voltage Characteristics

We compared the photovoltaic performance of the solid state devices with or without using compact TiO₂ layers. Figure 3 shows the current voltage (I-V) characteristics of a solid state TiO₂/P3HT device without using a compact TiO₂ layer in (a) semilogarithmic and in (b) linear scale. This kind of cell produced short circuit current density (I_{sc}) of 0.06 mA/cm², an open circuit voltage (V_{oc}) of 300 mV and a fill factor of 0.43.

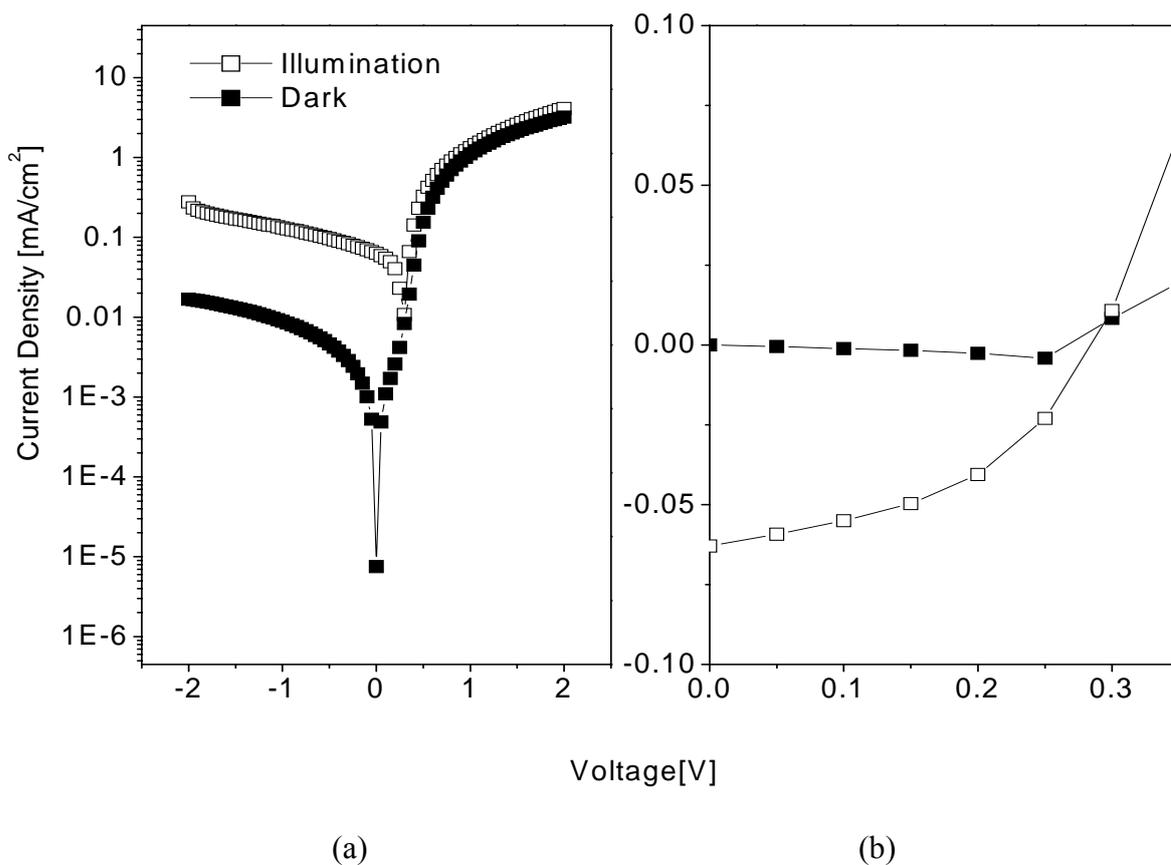


Figure 3. I-V characteristics of TiO₂/P3HT device without a compact TiO₂ layer (a) semilogarithmic (b) linear scale.

Figure 4 shows the I-V characteristics of a TiO₂/P3HT device with a compact TiO₂ layer. With the compact layer, the photovoltaic parameters improved to V_{oc} of 500 mV, I_{sc} of 0.4 mA/cm² and a fill factor of 0.5.

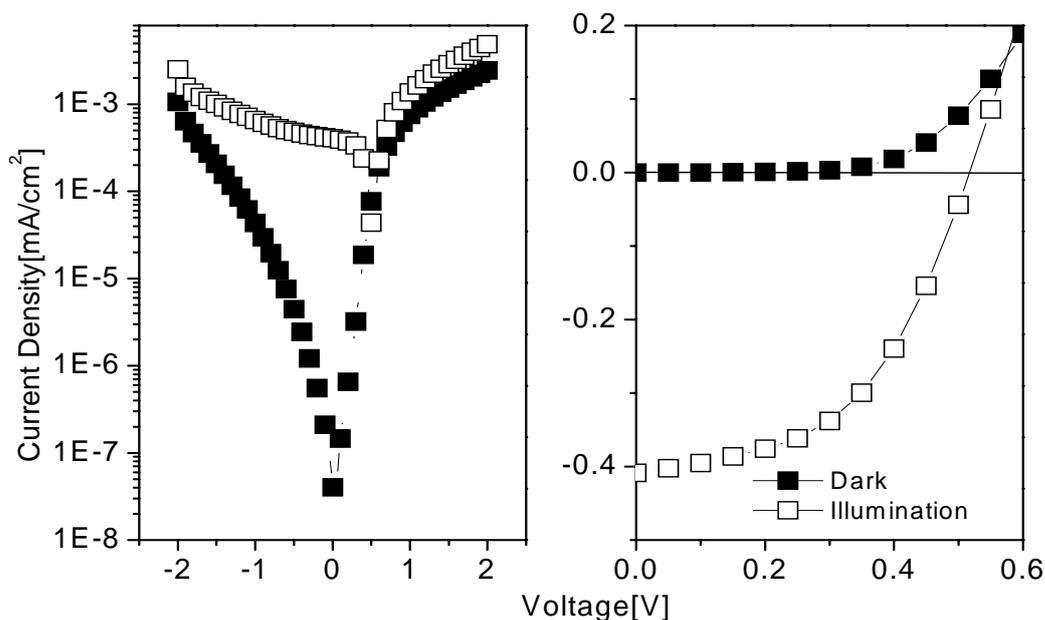


Figure 4. I-V characteristics of TiO_2 /P3HT device with a compact TiO_2 layer in (a) semilogarithmic (b) linear scale.

The comparison of the results on the photovoltaic performance with or without compact 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 TiO_2 layer on the dye sensitized solar cells, by introducing a ruthenium dye interlayer between nanoporous TiO_2 and P3HT. We prepared two kinds of cells (i) with dye but without a compact TiO_2 layer, (ii) with dye and with a compact TiO_2 layer. Figure 5 shows the former case. This kind of cell produced an I_{sc} of 0.09 mA/cm^2 , a V_{oc} of 550 mV and a fill factor of 0.3 .

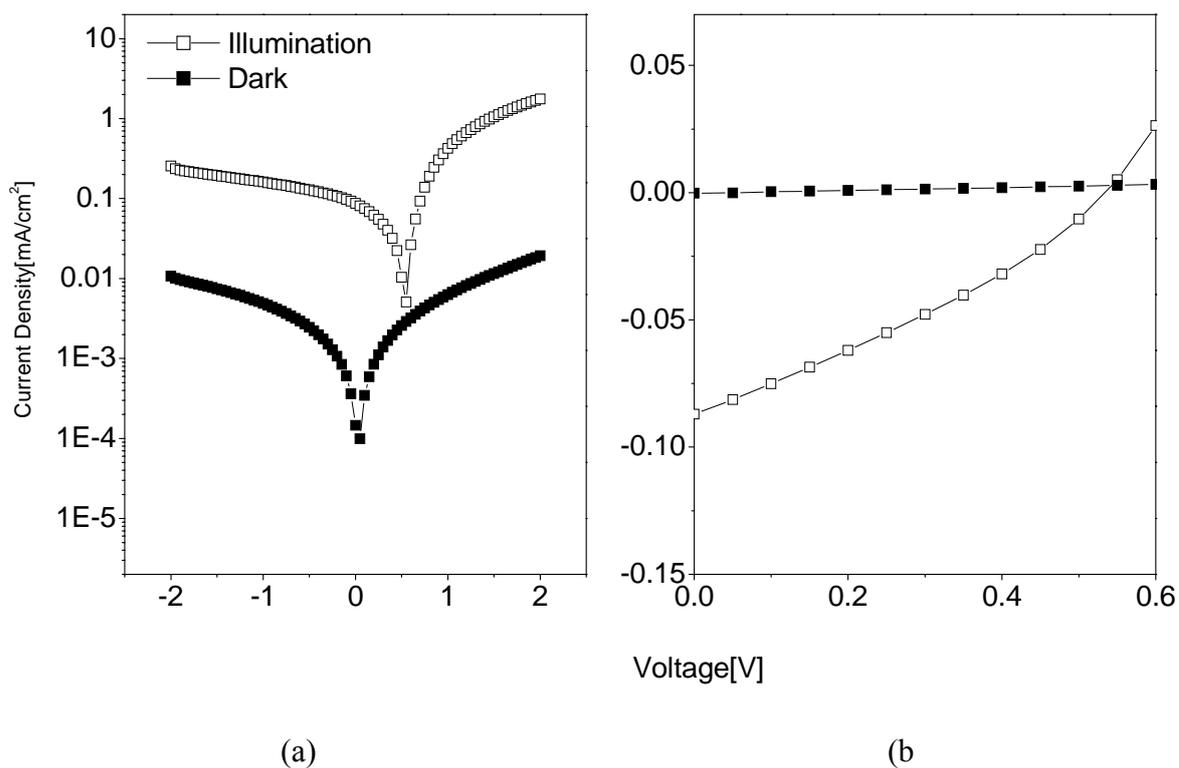
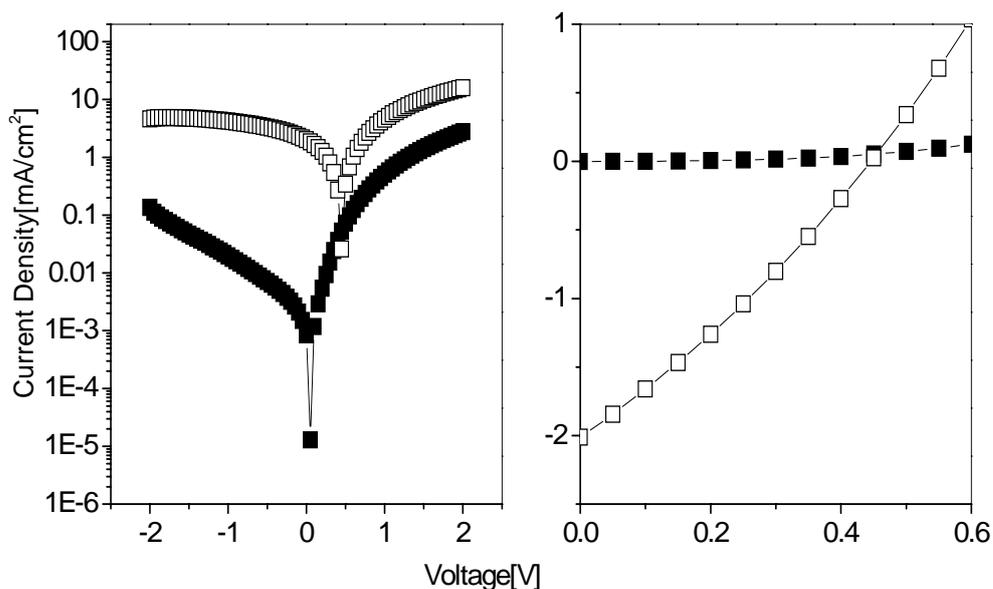


Figure 5. I-V characteristics of a $\text{TiO}_2/\text{P3HT}$ device with a dye but without a compact TiO_2 layer in (a) semilogarithmic scale (b) linear scale.

By employing the compact 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 mA/cm^2 and a fill factor of 0.3. Particularly, the improvement of the short circuit current from 0.4 mA/cm^2 to 2 mA/cm^2 is remarkable.



(a)

(b)

Figure 6. I-V characteristics of a TiO₂/P3HT device with a dye interlayer and with a compact TiO₂ 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 TiO₂ layer had an IPCE response below 0.1 % (not shown). The cells with compact TiO₂ 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 TiO₂ and P3HT. This enhancement in the IPCE is mainly attributed to the additional absorption offered by the ruthenium dye.

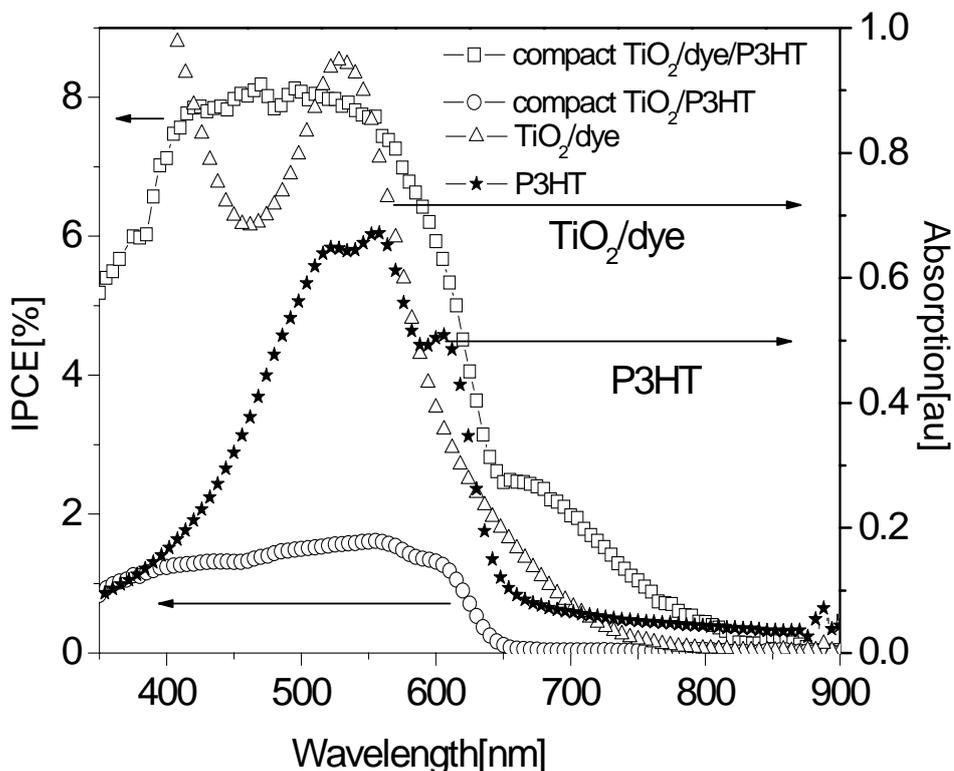


Figure 7. IPCE of $\text{TiO}_2/\text{dye}/\text{P3HT}$ and $\text{TiO}_2/\text{P3HT}$ devices with a compact TiO_2 layer (left y axis), and absorption spectra of TiO_2/dye and P3HT (right y axis).

4. Conclusions

We realized hybrid solid state devices fabricated from compact TiO_2 and nanoporous TiO_2 electrodes as electron transporting material and P3HT as organic hole transport material. We investigated the influence of compact 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 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 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.

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