Solid-state organic/inorganic hybrid solar cells based on conjugated polymers and dye-sensitized TiO$_2$ electrodes

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Abstract

Several efforts on using a dye-sensitized TiO$_2$ nanocrystalline solar cell (nc-DSC) by replacing the liquid electrolyte with a solid-state analogy (by either a polymer electrolyte or a hole conducting material) intend to eliminate practical problems with sealing and degradation. Polymeric materials that behave as hole conductors are of practical interest as replacements for the liquid electrolyte, since they are inexpensive and can be tailored chemically to fit a wide range of purposes. In this report, all solid-state organic/inorganic hybrid dye-sensitized solar cells were fabricated based on a bi- and tri-layer device concept using a transparent nanocrystalline TiO$_2$ layer as the electron acceptor and transport layer, a surface-adsorbed RuL2(NCS)/TBA (2:2) dye complex for light absorption and electron injection to the conduction band of TiO$_2$, and conjugated polymers as for the transport of holes to the back contact electrode. Comparative results of *I–V* characteristics, energy or power conversion efficiencies, as well as the surface network morphology of these films by atomic force microscope (AFM) will be discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photovoltaic; Dye-sensitized nc-TiO$_2$; Polythiophene; Metal/semiconductor interfaces

1. Introduction

Although the dye-sensitized TiO$_2$ nanocrystalline photoelectrochemical solar cells show excellent power conversion performance ($>10\%$) [1–3], their commercial applications is still limited due to stability problems (like evaporation of the electrolyte, degradation of the electrolyte or of the dye) as well as technological aspects of the large module production using a liquid electrolyte.

Various approaches have been reported in the literature as replacements for the liquid electrolyte, like a polymer gel electrolyte that conduct ions [4], inorganic materials such as p-type CuI, CuSCN, as well as organic hole conductors such as triphenyldiamine (TPD) or polypyrole [5–9]. Bach et al. [10] used an amorphous, organic hole transport material (HTM) to replace the electrolyte, in which positive charges are transported by hopping processes. Furthermore, p-type semiconducting polymers that accept holes from the dye cation are potential candidates for replacing the liquid electrolytes [5–8,10]. In order to realize this, several requirements have to be fulfilled [11]. In principle, the dye can also be replaced by the semiconducting polymer layer [12]. In such a bilayered device, the polymer fulfills the combined function as a sensitizer and as a hole transport layer. This implies a number of additional requirements for the polymer component as light absorbing layer [11].

In this work we realized dry, solid state TiO$_2$ solar cells using conjugated polymers both in the role of the hole conductor as well as in the dual role of dye/hole conductors.

2. Experimental

Fig. 1 shows the device configuration of a hybrid solid-state solar cell together with the chemical structures of the materials used. Films of nanocrystalline TiO$_2$ on ITO or SnO$_2$:F coated glass substrates (sheet

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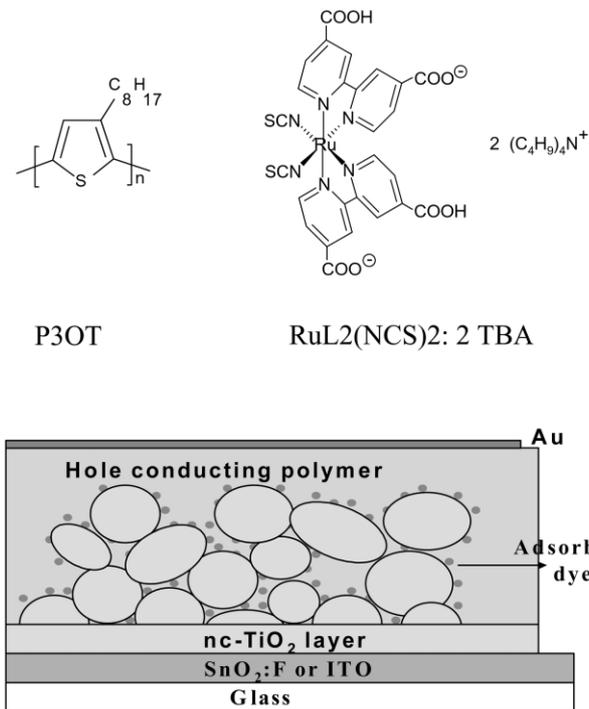*E-mail address:* dgebeyehu@yahoo.com (D. Gebeyehu).

P3OT   RuL2(NCS)2: 2 TBA

Fig. 1. Schematic diagram of the device configuration and molecular structures of the materials used.

resistance of 13 Ω/square) were prepared by doctor blading a paste from the Solaronix Co. (colloidal anatase, particle size of approx. 13 nm) with an active area of 5 mm^2. The above layers of the paste were then sintered for 30 min at 450°C in the oven and soaked with RuL2(NCS)2:2 TBA dye from Solaronix Co. used as sensitizer for these layers. Subsequently, a hole transport layer was applied by spin-coating films of poly (3-octylthiopehene) (P3OT) from toluene solution (10 mg in 1 ml of toluene). The thickness of the highly transparent nanocrystalline TiO$_2$ layers was approximately 2 μm, while the thickness of the hole transporting layers on top of the TiO$_2$ was typically in the range of 100–150 nm, as determined by Dektak measurements.

After an additional drying step, the top electrode gold (Au) was deposited by vacuum deposition. The current–voltage (*I–V*) characteristics were measured with a Keithley SMU 2400 Source Meter measurement unit in argon atmosphere under illumination through the ITO or SnO$_2$:F side by a white light source solar simulator. The incident light intensity was measured using an AM 1.5 calibrated single-crystal Si Photodiode. The surface network morphology of these film layers was examined with an atomic force microscope (AFM) in contact mode.

3. Results and discussion

The overall energy conversion efficiency η_e, has been calculated using the equation
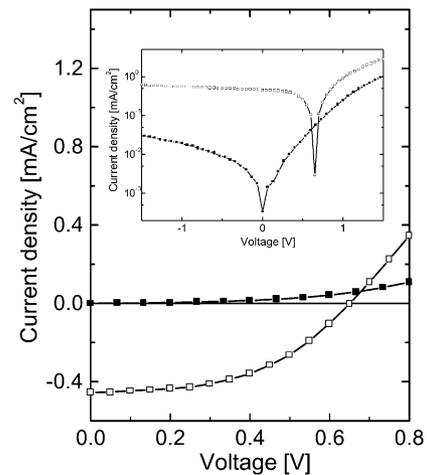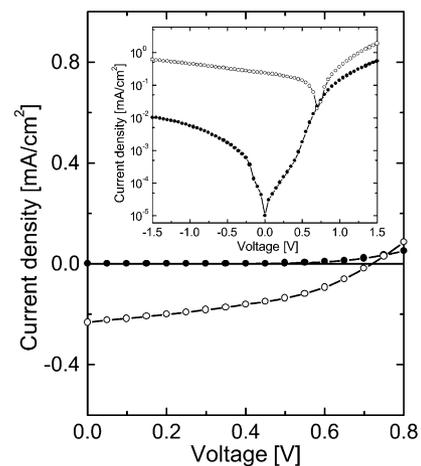
Fig. 2. *I–V* characteristics comparison of (a) SnO$_2$:F/nc-TiO$_2$/Ru-dye/P3OT/Au (solid squares, dark; open squares, illuminated with 80 mW/cm^2) and (b) ITO/nc-TiO$_2$/P3OT/Au (solid circles, dark; open circles, illuminated with 80 mW/cm^2) of hybrid solar cells in a linear scale. The inset is a logarithmic plot of the *I–V*.

$$\eta_e = (V_{oc}(V) \times I_{sc}(A/cm^2) \times FF)/P_{inc}(W/cm^2)$$

under different intensities, where V_{oc}, I_{sc}, FF and P_{inc} are the open circuit potential, short circuit current, fill factor and incident light power, respectively. We determine the value of the fill factor of the device, FF, by calculating the area of the maximum power rectangular area under the *I–V* curve in the 4th quadrant. Therefore, the filling factor is given by
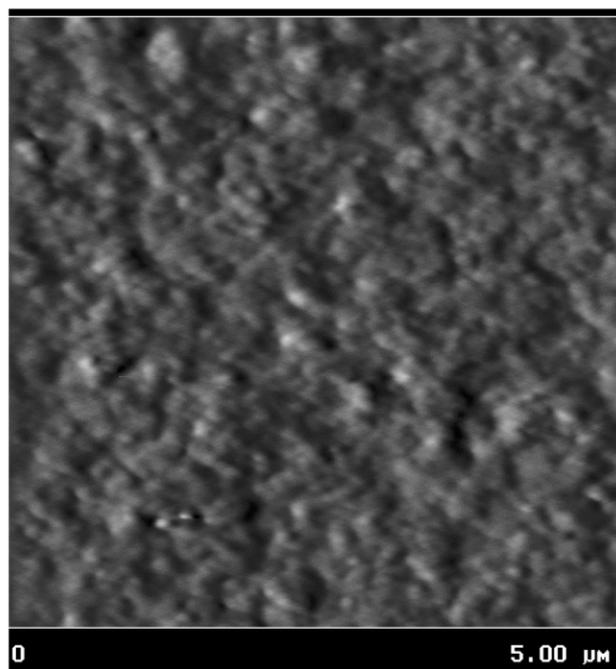
$$FF = (V_{max} \times I_{max})/(V_{oc} \times I_{sc}),$$

where V_{max} and I_{max} are the voltage and current, respectively, at the point of maximum power output.

The performance of photovoltaic devices from SnO$_2$:F/nc-TiO$_2$/Ru-dye/P3OT/Au and ITO/nc-TiO$_2$/P3OT/Au are compared and discussed in Fig. 2a,b by plotting the *I–V* characteristics in a linear and
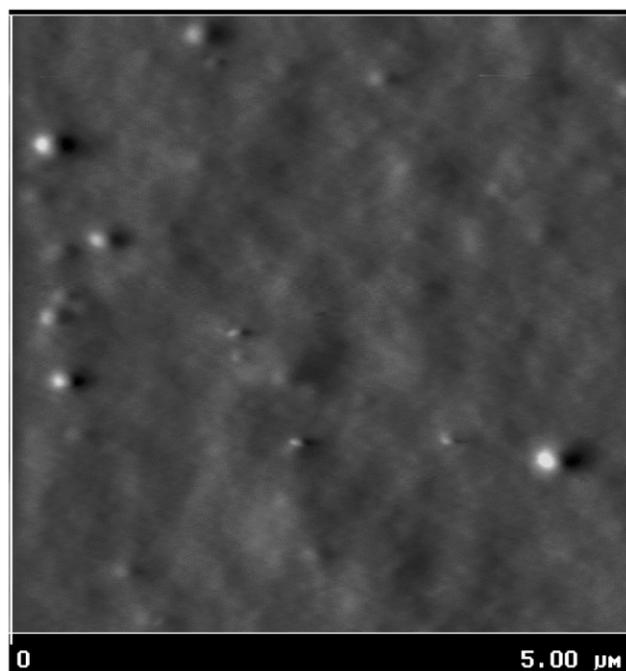
(a)

(b)

Fig. 3. AFM images of (a) nc-TiO$_2$/Ru-dye/P3OT and (b) nc-TiO$_2$/P3OT.

logarithmic scale, respectively. The characteristic values of the three-layered device in Fig. 2a are $V_{oc} \sim 650$ mV, $I_{sc} \sim 450$ μA/cm^2 and a fill factor $FF \sim 0.44$ under white light illumination with 80 mW/cm^2. The rectification of this device is ~ 15 at ± 1.5 V in the dark. The

I–V characteristics of the bilayered device without the dye (Fig. 2b) are $V_{oc} \sim 700$ mV, $I_{sc} \sim 230$ μA/cm^2 and a fill factor $FF \sim 0.37$ under white light illumination at 80 mW/cm^2. The rectification of this device is ~ 17 at ± 1.5 V in the dark. The overall energy conversion efficiency, η_e for the nc-TiO$_2$/Ru-dye/P3OT and nc-TiO$_2$/P3OT solid-state hybrid solar cells was calculated with 0.16 and 0.08% under white light solar simulator at 80 mW/cm^2, respectively.

Fig. 3 illustrates the surface morphology of (a) nc-TiO$_2$/Ru-dye/P3OT, (b) nc-TiO$_2$/P3OT films as determined by atomic force microscope in the contact mode. According to AFM images, the nc-TiO$_2$/Ru-dye/P3OT films show a very homogeneous surface (RMS surface roughness of approx. 4.4 ± 0.8 nm) without pores or pinholes. In contrast, Fig. 3b suggests a less smooth surface for nc-TiO$_2$ /P3OT films with RMS surface roughness of approximately 6 ± 0.85 nm. Deep holes or large area defects are not detected for the polymer films on top of the TiO$_2$ and therefore, shunts should be no major problem of the photovoltaic devices which is in good agreement with the results from *I–V* measurements.

4. Conclusion

We have realized hybrid solid-state solar cells fabricated from inorganic nanoparticles as electron transporting material and an organic hole transport materials with photoexcited dye molecules as absorber and electron injector material. These devices show open circuit voltages up to 650 mV and short circuit currents up to 450 μA/cm^2 under AM1.5 simulated solar radiation at 80 mW/cm^2. Under these illumination conditions, the highest overall energy conversion efficiency, η_e, was found to be 0.16% for the device consisting of nc-TiO$_2$/Ru-dye/P3OT/Au. Further optimization of the complicated interpenetrating network structure for the three components (organic dye, polymeric hole conductor, inorganic nc-TiO$_2$) is expected to enhance the efficiencies. Also, the energetic mismatch between the dye cation energy level and the positive polaronic energy level of the conjugated polymer semiconductor shall also be engineered in future work.

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