

Photovoltaic characterization of hybrid solar cells using surface modified TiO₂ nanoparticles and poly(3-hexyl)thiophene

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Abstract

We report on the photovoltaic performance of bulk heterojunction solar cells using novel nanoparticles of 6-palmitate ascorbic acid surface modified TiO₂ as an electron acceptor embedded into the donor poly(3-hexyl)thiophene (P3HT) matrix. Devices were fabricated by using P3HT with varying amounts of red TiO₂ nanoparticles (1:1, 1:2, 1:3 *w-w* ratio). The devices were characterized by measuring current–voltage characteristics under simulated AM 1.5 conditions. Incident photon to current efficiency (IPCE) was spectrally resolved. The nanoscale morphology of such organic/inorganic hybrid blends was also investigated using atomic force microscopy (AFM).

1. Introduction

Solar cells have attracted increasing attention over the last few decades as a viable alternative for replacing diminishing fossil fuels [1]. High efficiencies above 20% have been achieved by monocrystalline silicon solar cells, however their production cost and energy consumption during the fabrication process are quite high. Therefore, the development of inexpensive solar cells is of growing interest [2–4]. Organic, polymeric based photovoltaics have been considered as a new alternative photovoltaic technology due to their flexibility, light weight, low-cost fabrication, easy integration into a wide variety of devices, and due to the tunable properties of organic materials [5]. However, the performance of polymer based devices is low compared to inorganic solar cells [6]. Charge transport, limited exciton diffusion length, weak absorption coefficients and nanoscale morphology can be seen as possible reasons for the low efficiencies of polymer based photovoltaic devices [7]. The strategy of using interpenetrating networks of donor (electron donating and hole transporting) and acceptor (electron accepting and

transporting) materials has been introduced to create an interface between the donor/acceptor every few tens of nanometers [8–10]. This can help to overcome the limitation of exciton diffusion length. The bulk heterojunction concept can be achieved by blending not only two organic semiconductors but also organic and inorganic semiconductors. Inorganic semiconductors can be manufactured as nanoparticles using colloidal synthesis routes [11–13]. Blends of inorganic and organic semiconductors cast from co-solutions form bulk heterojunctions. These are denoted as ‘hybrid solar cells’. A hybrid solar cell comprises both organic and inorganic semiconductors, combining the unique properties of inorganic semiconductors together with the film-forming properties of polymers [13, 14]. Inorganic nanoparticles have several advantages such as size tunability and high absorption coefficients. Several studies have been performed to investigate hybrid solar cells using nanoporous metal oxide electrodes [15–17] or nanocrystal/conjugated polymer blend approaches using inorganic semiconductors such as TiO₂ [18], ZnO [19], CdSe [13, 14], and CuInS₂ [11].

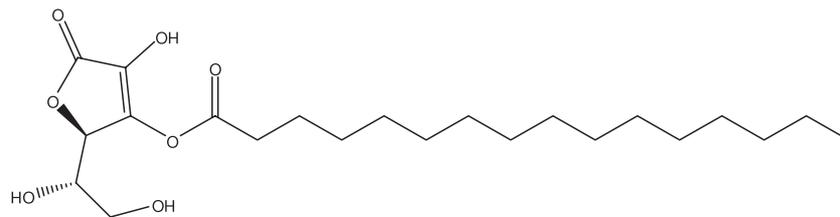


Figure 1. Chemical structure of 6-PAA.

In this study, we report on hybrid solar cells based on surface modified TiO_2 nanoparticles with 6-palmitate ascorbic acid (6-PAA) and poly(3-hexyl)thiophene (P3HT). The absorption spectrum of surface modified TiO_2 nanoparticles with 6-PAA is significantly red shifted compared to unmodified TiO_2 nanoparticles due to the formation of a charge transfer complex between TiO_2 and 6-PAA. The morphology, photovoltaic performance, and incident photon to current efficiency (IPCE) performance of such hybrid solar cells will be discussed.

2. Experimental details

2.1. Materials

Colloidal TiO_2 nanoparticles with an average diameter of 4.5 nm were prepared by the controlled hydrolysis of titanium tetrachloride, as described elsewhere [20]. The colloid concentration was determined from the concentration of the peroxide complex obtained after dissolving the colloid in concentrated HClO_4 [21].

Surface modification of colloidal TiO_2 nanoparticles was performed by mixing 20 ml of 0.15 M aqueous TiO_2 colloid solution with 6-PAA (0.248 g) dissolved in a mixture of methanol (4 ml) and toluene (10 ml). The chemical structure of PAA is shown in figure 1.

After shaking for a short time, a dark-red toluene phase containing the surface modified TiO_2 nanoparticles ($\text{TiO}_2/6\text{-PAA}$) separated from the aqueous phase. The obtained red toluene solution was poured into a large excess of methanol to remove free 6-PAA molecules. The surface modified TiO_2 particles were separated by centrifugation and redispersed in toluene. The residual methanol was removed by purging the solution with argon.

2.2. Photovoltaic device fabrication

As substrates, glass sheets of $1.5 \times 1.5 \text{ cm}^2$ covered with indium tin oxide (ITO), from Merck KG, Darmstadt, Germany, were used with an ITO thickness of about 120 nm and a sheet resistance $< 15 \Omega \text{ cm}^{-2}$.

The ITO was patterned by etching with an acid mixture of $\text{HCl}_{\text{konz}}:\text{HNO}_{3\text{konz}}:\text{H}_2\text{O}$ (4.6:0.4:5) for ~ 30 min. The part of the substrate that forms the contact is covered with Scotch tape, preventing etching. 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.

An aqueous solution of poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS) was spin coated onto the glass–ITO substrate and dried under a dynamic vacuum.

Blends of surface modified TiO_2 nanoparticles and P3HT were prepared by dissolving 1 wt% of P3HT in chlorobenzene and mixing with surface modified TiO_2 nanoparticles with 1:1, 1:2 and 1:3 ratios, respectively. The resulting blend was spin cast on top of PEDOT:PSS-covered ITO substrates at 2000 rpm. A thin film of lithium fluoride (LiF) and 100 nm of aluminum were thermally evaporated as top contacts.

All current–voltage (I – V) characteristics of the photovoltaic devices were measured (using a Keithley SMU 236) under argon in a dry glove box immediately after production. A Steuernagel solar simulator, simulating AM1.5 conditions, was used as the excitation source with an input power of 100 mW cm^{-2} white-light illumination.

2.3. Optical absorption and incident photon to current efficiency (IPCE) characterization

The absorption spectra of the TiO_2 colloids in water and the $\text{TiO}_2/6\text{-PAA}$ nanoparticles in toluene were recorded using a Perkin-Elmer Lambda 5 ultraviolet–visible (UV–vis) spectrophotometer.

The spectrally resolved photocurrent was measured using an EG&G Instruments 7260 lock-in amplifier. The samples were illuminated with monochromatic light from a xenon lamp. The incident photon to current efficiency (% IPCE) was calculated according to the following equation:

$$\text{IPCE}(\%) = \frac{I_{\text{sc}} * 1240}{P_{\text{in}} * \lambda_{\text{incident}}},$$

where I_{sc} ($\mu\text{A cm}^{-2}$) is the measured current under short-circuit conditions of the solar cell, P_{in} (W m^{-2}) is the incident light power, measured with a calibrated silicon diode, and λ (nm) is the incident photon wavelength.

2.4. Atomic force microscopy (AFM)

Atomic force microscopy studies were performed using Digital Instruments DIMENSION 3100 in the tapping mode.

3. Results and discussion

3.1. Absorption characteristics

The absorption of the TiO_2 nanoparticles changed after surface modification with 6-PAA. The absorption spectra of TiO_2

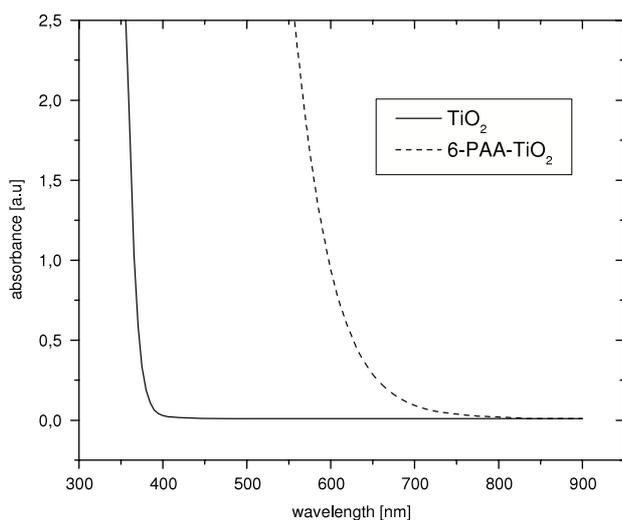


Figure 2. Absorption spectra of TiO_2 colloid in water (solid line), and $\text{TiO}_2/6\text{-PAA}$ in toluene (dashed line).

colloids in water and $\text{TiO}_2/6\text{-PAA}$ in toluene are shown in figure 2. The spectrum of the surface modified TiO_2 nanoparticles is red shifted compared to the unmodified TiO_2

nanoparticles. The absorption onset for the surface modified TiO_2 nanoparticles is around 650 nm compared to 380 nm for the unmodified TiO_2 nanoparticles. The significant red shift of the absorption onset for TiO_2 nanoparticles upon modification can be assigned to the formation of a charge transfer complex between the surface of the TiO_2 nanoparticles and 6-PAA, as described in the literature [22, 23].

3.2. Photovoltaic performance

$\text{TiO}_2/6\text{-PAA}$ nanoparticles were evaluated as electron acceptors in hybrid bulk heterojunction solar cells. Solar cells were investigated by varying the nanoparticle/polymer ratio. The current–voltage (I – V) characteristics of bulk heterojunction solar cells using red TiO_2 nanoparticles are shown in figure 3. Solar cells composed of pristine polymer in the active layer did not significantly generate photocurrent under illumination. Hybrid solar cells with 1:1 P3HT: $\text{TiO}_2/6\text{-PAA}$ ratio showed a short-circuit current density (I_{sc}) of 0.17 mA cm^{-2} and an open-circuit voltage (V_{oc}) of 450 mV with a fill factor (FF) of 0.26. As the P3HT: $\text{TiO}_2/6\text{-PAA}$ ratio was changed to 1:2, an I_{sc} of 0.2 mA cm^{-2} and a V_{oc} of 400 mV with a FF of 0.29 were observed. Finally, changing the ratio to 1:3 led to an I_{sc} of 0.4 mA cm^{-2} and a V_{oc} of 450 mV with a FF of 0.28.

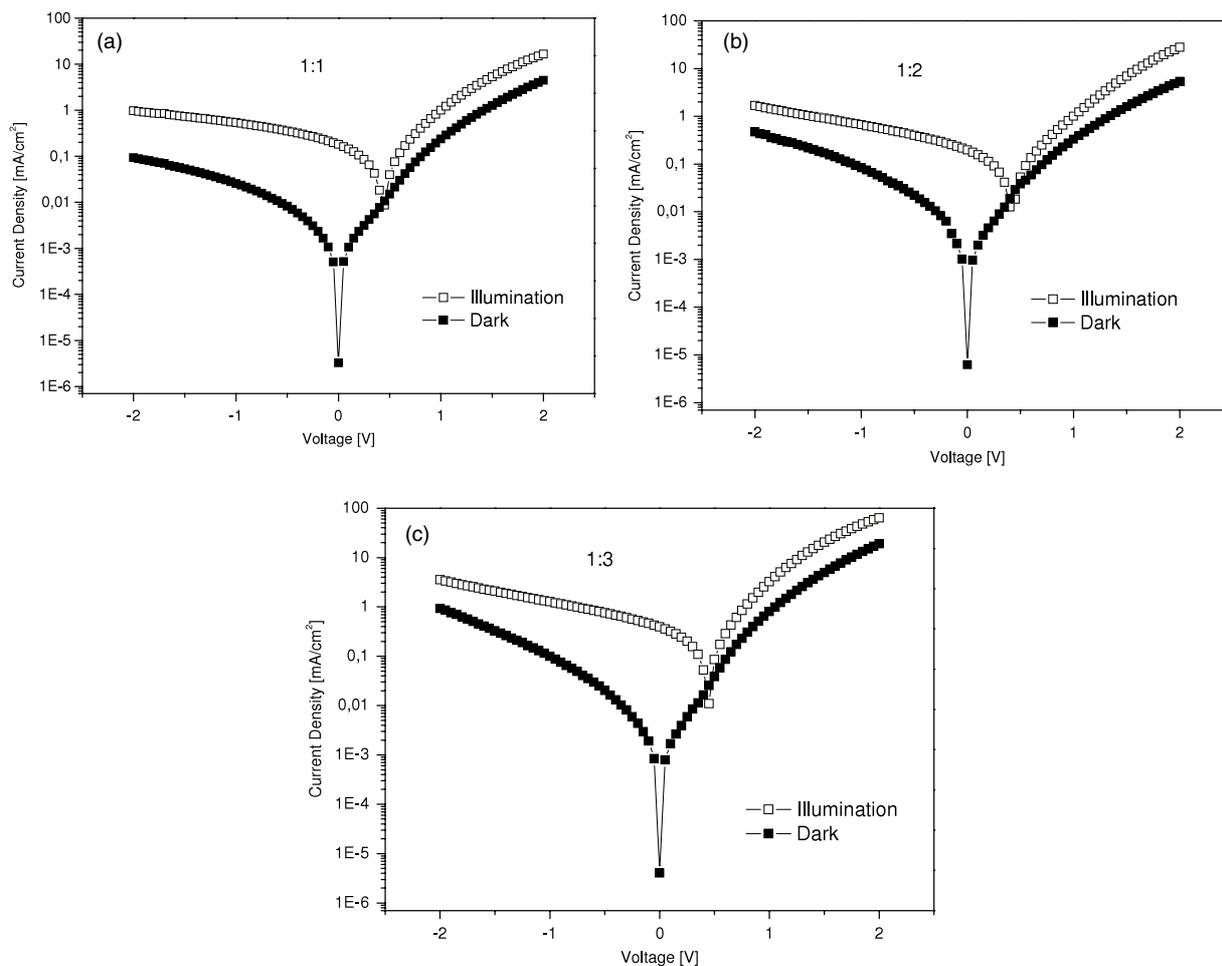


Figure 3. I – V characteristics of hybrid solar cells using P3HT and surface modified TiO_2 nanoparticles: (a) 1:1, (b) 1:2 and (c) 1:3 ratios, respectively.

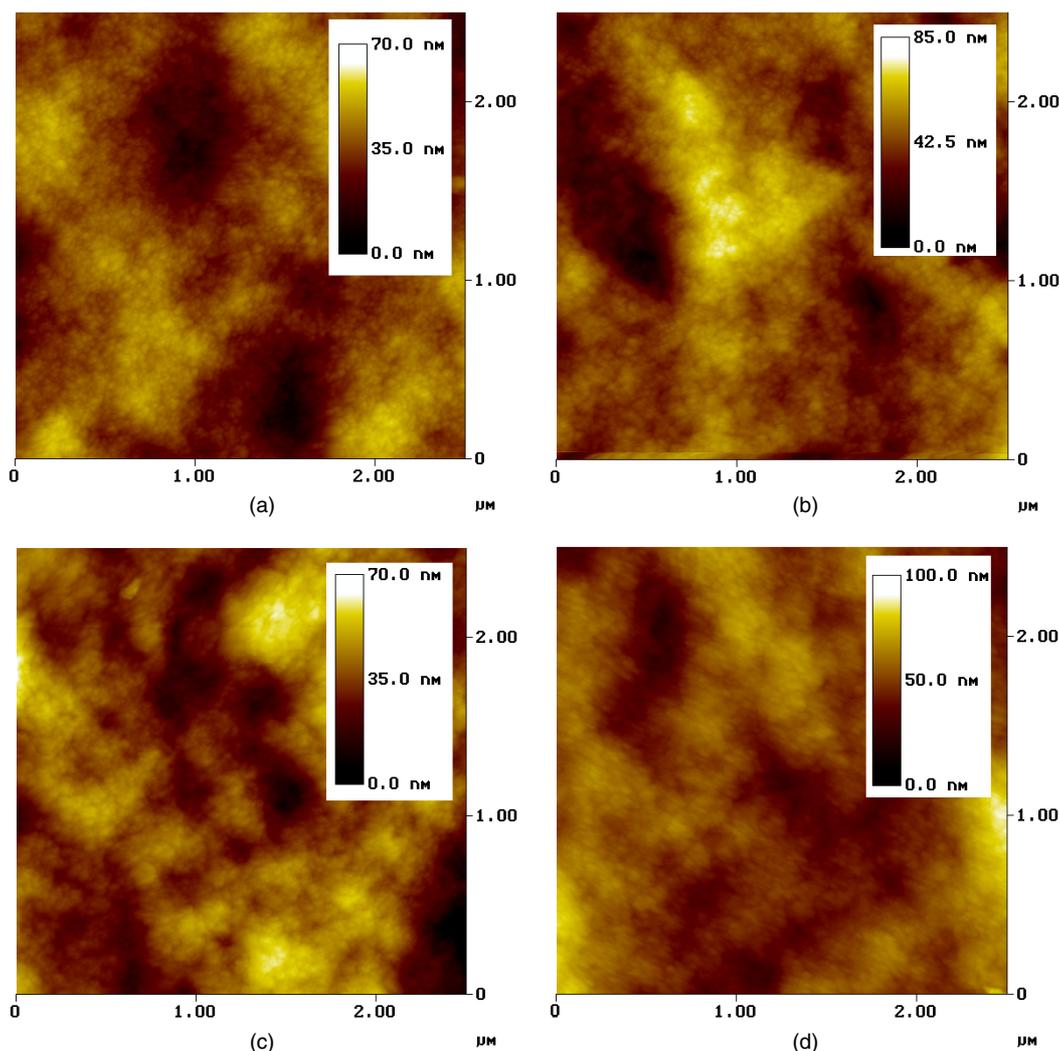


Figure 4. AFM images of (a) bare red TiO₂ film, (b) 1:1 blend, (c) 1:2 blend and (d) 1:3 blend.
(This figure is in colour only in the electronic version)

We have observed that, as the TiO₂/6-PAA ratio is decreased, the current increases slightly. The fill factor (FF) of the device also plays an important role in the overall low efficiency of the cell. The value of 0.28 here is indicative of the poor performance for these devices. In general, parallel and series resistances can account for the low FF. It has been demonstrated that the improvement in charge transport of the donor polymer can increase the fill factor of solar cells. The long side chains attached to this ligand will hinder electron transport from nanoparticles to nanoparticles. This certainly causes a series resistance due to low mobility.

3.3. Morphology of blends by atomic force microscopy (AFM)

The behavior of solar cells is analyzed via study of the nanomorphology of the active layer. The challenge in bulk heterojunction solar cells is to organize donor and acceptor phases. On the one hand their interfacial area has to be maximized [7, 9], while typical dimensions of phase separation shall stay within the exciton diffusion length (of the order of 10 nm). On the other hand, continuous, preferably undisturbed

pathways for the transport of charge carriers to the respective electrodes must be ensured.

To correlate the morphology of the solar cells to photovoltaic performance, we performed an AFM study on the P3HT:red TiO₂ blends. Figure 4 shows the images obtained by AFM for P3HT:red TiO₂ films for three different compositions (1:1, 1:2, 1:3).

As can be seen from the figures, all three films indicate rough surfaces, which might explain the low efficiencies. The coarse phase separation is clearly visible. As shown in [6, 7], the coarse nanomorphology is unfavorable for high efficiency.

3.4. Optical absorption and incident photon to current efficiency (IPCE)

Comparing the spectral response of the solar cells and the optical absorption spectra of the components of the devices, information on the charge-generation mechanism can be obtained. The IPCE percentage is the percentage of electrons, measured under short-circuit current conditions, that are related to the number of incident photons. It is used to obtain

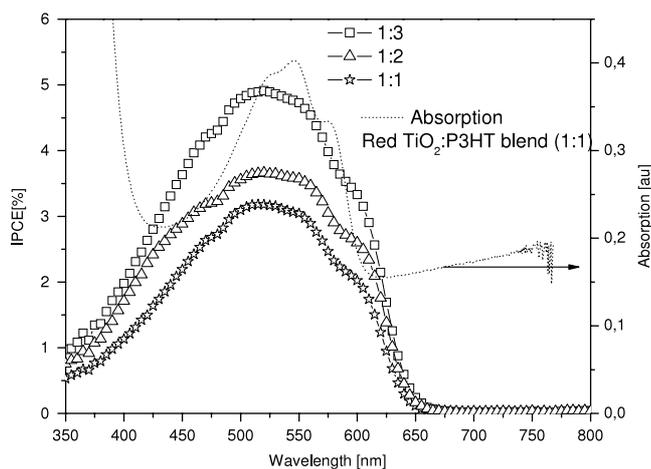


Figure 5. IPCE (left-hand scale) spectra of the hybrid solar cells and absorption (right-hand scale) of red TiO_2 /P3HT blends.

information on the numbers of photons of different energies that contribute to charge generation in the solar cell [24]. Figure 5 shows the IPCE spectra of hybrid solar cells that are investigated in this study.

The IPCE percentage plot exhibits a maximum photocurrent contribution of about 5% at around 520 nm. It is noted that the spectrum lies over a wide range of wavelengths (350–650 nm). It can be seen clearly that optical absorption and IPCE spectra both match.

4. Conclusions

We have studied the performance of surface modified TiO_2 nanoparticle and P3HT nanocomposite solar cells as a function of the surface modified TiO_2 concentration. As a novel surface ligand on TiO_x nanoparticles, we used palmitate ascorbic acid. The photovoltaic performance of these solar cells was remarkably enhanced for the surface modified TiO_2 :P3HT nanocomposite solar cell compared to the pristine P3HT cell. For efficient charge transfer, the lowest unoccupied molecular orbital (LUMO) of the electron donor should be energetically located above the conduction band of TiO_2 as an electron acceptor. It was electrochemically difficult to determine the energy levels of these surface modified TiO_2 nanoparticles and/or to compare how much it was shifted compared to commercially available TiO_2 nanoparticles absorbing in the UV region. However, the remarkable increase in the short-circuit density of surface modified TiO_2 :P3HT nanocomposite solar cells compared to pristine P3HT cells might be explained by the photoinduced charge transfer that occurred between the donor P3HT and the acceptor surface modified TiO_2 . Nanocomposite solar cells show moderate efficiencies, and further optimization is required for more efficient devices.

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