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Poly(3-hexylthiophene):TiO$_2$ nanocomposites for solar cell applications

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Abstract

The properties of organic/inorganic poly(3-hexylthiophene) (P3HT):TiO$_2$ nanocomposite films and nanocomposite based solar cells as a function of TiO$_2$ concentration and the solvent used for the film fabrication were studied. For low nanoparticle concentration (20–30%) the device performance was worse compared to pure P3HT, while for nanoparticle concentration of 50% and 60% significant improvements were obtained. P3HT photoluminescence quenching in 600–800 nm spectral region changes by a factor of two for the increase in TiO$_2$ concentration from 20% to 60%, while the AM1 power conversion efficiency increases $\sim$35 times. Photoluminescence quenching and solar cell efficiency were found to be strongly dependent not only on nanoparticle concentration but also on the solvent used for spin-coating. The changes in the film and device properties were explained by the change in the film morphology. For optimal fabrication conditions, external quantum efficiency up to 15% and AM1 power conversion efficiency of 0.42% were obtained.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Organic/inorganic nanocomposites are very promising for applications in devices such as light emitting diodes, photodiodes, photovoltaic cells, and gas sensors [1]. Since the properties of a nanocomposite film can be easily changed by varying its composition, such materials are highly versatile, while their fabrication shares the same advantages with traditional organic device technology, such as low cost production and the possibility of device fabrication on large area and flexible substrates. Applications of different organic–inorganic nanocomposites to organic solar cells [2–9] have been reported. Typically, the performance of a nanocomposite solar cell is improved compared to a pristine polymer one. External quantum efficiency (EQE) over 54% and AM 1.5 power conversion efficiency of 1.7% were achieved in poly(3-hexylthiophene) (P3HT):CdSe nanocomposite solar cells [6]. An EQE up to 45% and power conversion efficiency of 0.49% has been reported for a PbS quantum dot sensitized organic solar cell with nanocrystalline TiO$_2$ electrode. However, the majority of the work on nanocomposite solar cells still reports efficiencies below 0.1% [2, 5, 7]. Huisman et al [2] reported 0.06% efficiency in TiO$_2$/poly(3-octylthiophene) solar cells. Breeze et al [8] reported an EQE of 6.4% and cell parameters corresponding to a power conversion efficiency of 0.002% for a cell consisting of a junction between a TiO$_2$ nanoparticle layer and poly(2-methoxy,5-(2'-ethyl-hexyloxy)-p-phenylenevinylene) (MEH-PPV) sandwiched between indium tin oxide (ITO) and Au electrodes. In order to improve the efficiency of TiO$_2$/polymer solar cells, it is necessary that the photogenerated excitons in the polymer reach the interface with TiO$_2$ and successfully dissociate. One of the common methods to improve the exciton dissociation in organic photovoltaics is the use of bulk...
heterojunction structures. Bulk heterojunction TiO₂-poly(2-methoxy-5-(3′,7′-dimethyl-octyloxy)-p-phenylene vinylene) (MDMO-PPV) photovoltaic cells have been reported, with EQE reaching 11% and power conversion efficiency of 0.18% for 20% TiO₂ [9]. While this result is an improvement over the results obtained with two layer architecture, further work is needed to improve the performance of these devices and increase the exciton dissociation and charge collection efficiency.

The performance of polymer–inorganic nanoparticle bulk heterojunction solar cells will be strongly dependent on the charge transport processes in organic–inorganic nanocomposites [10–13]. However, both increase [13] and decrease [10] in mobility with increased nanoparticle concentration have been reported. The contradictory results are most likely due to differences in fabrication techniques, as well as the different polymers and nanoparticles used. The fabrication conditions can significantly affect phenomena such as local electrical field enhancement and chain alignment and thus affect the carrier mobility within the layer and the device performance. It is well known that the properties of organic donor–acceptor blends and bulk heterojunction devices are strongly dependent on the film morphology [14, 15]. However, studies on the influence of the film morphology on the electrical and optical properties of the organic–inorganic nanocomposite films and the performance of nanocomposite based devices have been scarce [16, 17].

In this work, we investigate the influence of the nanoparticle concentration and the solvent used for the film preparation on the optical properties of P3HT:TiO₂ nanocomposite films and the performance of P3HT:TiO₂ based solar cells. The films were characterized using photoluminescence (PL) and atomic force microscopy (AFM). The solar cells were characterized by measuring I–V characteristics in the dark and under AM1 solar illumination and by determining the external quantum efficiency (EQE) as a function of wavelength. The solar cell structure (ITO/PEDOT:PSS (poly(ethylenedioxythiophene) blended with polystyrene sulfonic acid)/P3HT:TiO₂/Al) and the energy levels of the materials used according to [18–20] are shown in figure 1. The paper is organized as follows. In the following section, experimental details are given. In section 3, obtained results are presented and discussed. Finally, conclusions are drawn.

2. Experimental details

ITO glass substrates with surface sheet resistance ~10 Ω/square were supplied by China Southern Glass Holding Co. Ltd, Shenzhen, China. ITO glass substrates were cleaned in an ultrasonic bath using toluene, acetone, ethanol, and deionized water. PEDOT:PSS was obtained from Bayer AG; regioregular P3HT was purchased from Aldrich. TiO₂ nanoparticles with particle size 20–40 nm (solid spherical particles, anatase/rutile structures) were purchased from Nanopowder Enterprises. A 30 nm layer of PEDOT:PSS was spin-coated on cleaned ITO glass, followed by 24 h baking at 110 °C in a vacuum oven.

After the baking of PEDOT:PSS, ~100 nm thick pure P3HT or P3HT:TiO₂ films were spin-coated. In order to achieve sufficient concentration of P3HT to fabricate 100 nm thick films, the solutions were prepared in a heated ultrasonic bath (at 50 °C) to improve solubility. The films were then baked in a vacuum oven for 24 h at 110 °C. The Al electrode was then evaporated in high vacuum. The pressure during evaporation was of the order of 10⁻⁴ Pa.

The current–voltage characteristics were measured using a Keithley 2400 sourcemeter. For white light efficiency measurements, an Oriel 66002 solar simulator with AM1 filter was used. The light intensity was 100 mW cm⁻². For the external quantum efficiency measurement, an Oriel Cornerstone monochromator was used. Atomic force microscopy (topography and phase contrast) measurements were performed using a Digital Instruments Nanoscope III operating in dynamic mode. The room temperature photoluminescence was measured using an HeCd laser excitation source (325 nm) and Ar ion laser excitation source (514 nm). For both excitation wavelengths similar results were obtained for the characteristic two peak P3HT emission in the 550–800 nm spectral range.

3. Results and discussion

Photoluminescence quenching in a bulk heterojunction is a useful indication of the degree of success of exciton dissociation. Figure 2 shows the PL spectra of ~100 nm thick films for different concentrations of TiO₂ nanoparticles. It can be observed that even for low TiO₂ concentrations, such as 20%, significant PL quenching is obtained. With the
increase of TiO\(_2\) nanoparticle concentration, the PL is further quenched. The intensities of the PL spectra for films with 20\% and 60\% TiO\(_2\) differ by a factor two. The conductivity in the dark is also substantially improved for the composite films, but it does not show significant dependence on the TiO\(_2\) concentration. However, more significant difference can be observed in the performance of solar cells with different TiO\(_2\) concentration. The obtained results are summarized in table 1, while figure 3 shows a comparison between the EQEs for different nanoparticle concentrations. For low nanoparticle concentration (20\% and 30\%), the cell performance is inferior to that of the pure P3HT, in spite of the significant PL quenching. For 40\% nanoparticle concentration, the cell performance becomes comparable to that of pure P3HT, while for 50\% and 60\% TiO\(_2\) significant improvement is obtained. For nanoparticle concentrations higher than 70\%, the cell performance deteriorates, since it is not possible to produce good quality uniform films. The quenching of P3HT photoluminescence indicates that the excitons successfully dissociate at the P3HT:TiO\(_2\) interface. This is in agreement with the results obtained for TiO\(_2\):PPV poly(p-phenylenevinylene) composites [11]. When the TiO\(_2\) concentration was above 20 wt\%, most excitons dissociated at the interface of the polymer and nanocrystals, but the charge collection efficiency was limited by recombination [11]. Therefore, successful exciton dissociation is not sufficient to ensure good photovoltaic cell performance. It is necessary to prevent the recombination of separated charges in order to achieve good photovoltaic performance. For low TiO\(_2\) concentrations, it is possible that electrons will be trapped at the dead end conduction paths and recombine with the holes in the polymer. With increased nanoparticle concentration, it can be concluded from the decreased PL intensity that the exciton dissociation is further improved, but more significantly electron transport through the nanocrystal network without recombination with the holes in the polymer becomes more likely.

Exciton dissociation and charge transport in nanocomposite solar cells have been modelled for several material systems [11, 12, 21]. In nanocomposite solar cells containing either a nanoporous electrode/polymer junction or a nanoparticle/polymer bulk heterojunction, the electrons are injected from the polymer into the conduction band of the semiconductor, so that the polymer acts as a sensitizer and hole transport

Table 1. Comparison of P3HT:TiO\(_2\) based solar cells for different TiO\(_2\) concentrations.

<table>
<thead>
<tr>
<th>TiO(_2) conc (%)</th>
<th>(V_{OC}) (V)</th>
<th>(J_{SC}) (mA cm(^{-2}))</th>
<th>FF</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.8</td>
<td>0.325</td>
<td>0.230</td>
<td>0.059</td>
</tr>
<tr>
<td>20</td>
<td>0.3</td>
<td>0.129</td>
<td>0.274</td>
<td>0.012</td>
</tr>
<tr>
<td>30</td>
<td>0.24</td>
<td>0.191</td>
<td>0.269</td>
<td>0.013</td>
</tr>
<tr>
<td>40</td>
<td>0.38</td>
<td>0.531</td>
<td>0.344</td>
<td>0.076</td>
</tr>
<tr>
<td>50</td>
<td>0.46</td>
<td>1.896</td>
<td>0.321</td>
<td>0.274</td>
</tr>
<tr>
<td>60</td>
<td>0.44</td>
<td>2.759</td>
<td>0.356</td>
<td>0.424</td>
</tr>
<tr>
<td>70</td>
<td>0.34</td>
<td>0.505</td>
<td>0.396</td>
<td>0.067</td>
</tr>
</tbody>
</table>

In order to investigate the influence of the film morphology on the PL quenching and the photovoltaic cell performance, we prepared P3HT:TiO\(_2\) films by spin-coating using different solvents. It was shown that the performance of poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV)-C\(_{60}\) bulk heterojunction solar cells exhibits strong dependence on the solvent used [15]. In general, the performance of devices based on polymer blends is known to be strongly dependent on the film morphology, and the highest efficiencies are observed for devices with nanoscale phase separation [24]. Figure 4 shows the PL spectra of ~100 nm P3HT:TiO\(_2\) thin films with 60\% TiO\(_2\) concentration fabricated by spin-coating from different solvents. The performance of solar cells for 60\% TiO\(_2\) layer [22]. Electron transfer from poly(p-phenylenevinylene) and polythiophene derivatives to TiO\(_2\) has been confirmed by photoinduced absorption and photoinduced electron spin resonance (ESR) measurements [23]. The separated carriers (electrons in TiO\(_2\) and holes in the polymer) can either be collected at the electrodes or recombine at the polymer/nanoparticle interface [22]. It is likely that more than one recombination process or reaction species contributes to the recombination dynamics [21]. Recombination of the separated charges was found to be a serious problem limiting the efficiency of polymer–TiO\(_2\) nanoparticle composites [11]. The charge collection efficiency is dependent on the connectivity of the nanoparticle network and the distribution of the available paths [21]. Therefore, it is expected that the charge collection and thus overall device efficiency will be strongly dependent on the nanocomposite film morphology.

Figure 2. The photoluminescence spectra from P3HT:TiO\(_2\) layers for different TiO\(_2\) concentrations.

Figure 3. The comparison between external quantum efficiencies (EQEs) of nanocomposite (40\%, 50\%, and 60\% TiO\(_2\)) and pure P3HT cells. The inset shows the corresponding dark current densities versus voltage.
Chlorobenzene and spin-coating conditions can affect the aggregation of P3HT films, however, no significant effect of solvent on the solar cell performance was observed, and for all solvents used an efficiency of 0.06–0.08% was obtained. It can be observed that the strongest PL quenching and the highest cell efficiency of 0.06–0.08% was obtained. For pure P3HT films, however, no significant effect of solvent on the cell performance was observed, and for all solvents used an efficiency of 0.06–0.08% was obtained. It can be observed that the strongest PL quenching and the highest cell efficiency is obtained for xylene. However, the PL of films spin-coated from chlorobenzene, and yet cells fabricated from chlorobenzene solutions exhibit ~5 times higher power conversion efficiency and ~2 times higher EQE.

Therefore, it can be concluded that the solvent used affects both the PL quenching and the recombination of separated charges, which is likely due to the different film morphologies caused by the different solvents. It is known that the solvent and spin-coating conditions can affect the aggregation of the polymer chains [25], as well as the quality of polymer–metal contacts [26]. In order to examine the influence of the solvent used on the film morphology, films spin-coated from different solvents were examined using dynamic mode AFM (topography and phase contrast). Phase contrast imaging enables mapping of the variations in the composition of the film surface [27]. Phase contrast imaging is based on the principle that the phase lag of the tip depends on the material [27]. The measurement of the phase lag between the tip and the excitation signal while the amplitude is kept constant enables detection of the variation in the material properties [27]. Thus, phase contrast imaging enables us to investigate the degree of mixing and the domain sizes for the two components of the nanocomposite films. The results obtained (for 60% TiO2 concentration) are shown in figure 6. The measurements were performed after baking the layers spin-coated on the top of baked PEDOT-PSS, i.e. the same preparation conditions used for devices. The solvent affects the surface roughness of the films, but no direct correlation is observed between the surface roughness and the solar cell performance. Excessive surface roughness which would result in poor electrode contact, pinholes, and defects (such as in the case of the film with 70% TiO2) should be avoided, but small variations in the surface roughness do not appear to have significant effect on the device performance. The rms surface roughness values are similar for all films, and vary from 20.5 nm for THF to 29.6 nm for xylene. No significant differences can be observed from the topography images. However, phase contrast images reveal that the mixing between P3HT and TiO2 is strongly dependent on the solvent used. For the films prepared from chlorobenzene and xylene, better mixing between TiO2 and P3HT was obtained compared to the films spin-coated from chloroform and THF. The large number of small domains obtained in the former case yield a large interface and improved exciton dissociation.

The results obtained are similar to those reported for MEH-PPV-C60 cells [15], where the difference between the performance of the cells fabricated from xylene, dichlorobenzene, chlorobenzene, THF, and chloroform was explained by preferential solvation of π-electron conjugated segments in aromatic solvents. Unlike the results reported by Liu et al [15], our results did not show any significant variation of the performance of pure P3HT cells on the solvent used for film fabrication. Therefore, the mechanism proposed by Liu et al [15] is probably not the most significant factor in determining the performance of P3HT:TiO2 solar cells. The main difference between the films prepared from different solvents is the degree of mixing between P3HT and TiO2, which is dependent on the solvating power of the solvent used and on the solvent evaporation rate. It is known that the solvent evaporation rates influence the surface morphology of polymer films [28]. THF and chloroform have one order of magnitude lower evaporation rates than xylene. Table 2. Comparison of solar cells with 100 nm P3HT:TiO2 layer prepared from different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>V_{oc} (V)</th>
<th>ISC (mA cm$^{-2}$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>0.34</td>
<td>0.246/4</td>
<td>0.396</td>
<td>0.033</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>0.38</td>
<td>0.646/4</td>
<td>0.358</td>
<td>0.086</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>0.44</td>
<td>1.192/8</td>
<td>0.341</td>
<td>0.175</td>
</tr>
<tr>
<td>Xylene</td>
<td>0.44</td>
<td>2.758/6</td>
<td>0.356</td>
<td>0.424</td>
</tr>
</tbody>
</table>

Figure 4. The photoluminescence spectra from P3HT:TiO2 layers spin-coated from different solvents.

Figure 5. The external quantum efficiency (EQE) of P3HT:TiO2 cells with P3HT:TiO2 films spin-coated from different solvents.
Figure 6. AFM topography (left) and phase contrast (right) images of P3HT:TiO₂ films spin-coated from different solvents: (a) chloroform, (b) THF, (c) chlorobenzene, and (d) xylene.
magnitude higher vapour pressure compared to xylene [28], and hence evaporate significantly faster than xylene and chlorobenzene. Also, since the solvating power of aromatic solvents like xylene and chlorobenzene for P3HT is higher, this could lead to a more extended polymer chain in the solid state and thus to different film morphology.

It should be noted that, while the best efficiencies are generally obtained for the nanoscale phase separation, the solvent resulting in the nanoscale phase separation may be different for different material systems. Arias et al [24] obtained improved performance for their polymer bulk heterojunction cell when chloroform was used as a solvent compared to the cell prepared from xylene solution. However, in their case, the films prepared from chloroform exhibited smaller scale phase separation compared to the films prepared from xylene [24]. Therefore, the general guideline for improving the efficiency of composite or blend solar cells is to achieve the phase separation on the nanoscale in order to improve the exciton dissociation efficiency which would otherwise be poor due to the short exciton diffusion length. The morphology of the composite or blend layer is strongly solvent dependent [15, 24], but the optimal solvent for the small scale phase separation may differ for different materials used. Nanoscale phase separation as a rule results in efficient exciton dissociation, but this is not sufficient for the fabrication of efficient photovoltaic cells due to charge collection limitations [11]. Thus, the cells with 20% TiO2 show efficient photoluminescence quenching, but poor photovoltaic performance, in agreement with the previously reported results [11]. The solar cell performance can be significantly improved by optimizing the TiO2 concentration to improve the charge collection by improving the connectivity of the nanoparticle network. However, further work is needed in order to improve the performance of these devices, mainly by inhibiting the recombination of the separated charges. This can be achieved either by changing the polymer or nanoparticles used, or by surface modifications of the nanoparticles or the use of core-shell nanoparticles. It has been shown that the performance of nanostructured TiO2 cells can be improved with a suitably chosen recombination barrier coatings [29, 30].

4. Conclusions

We have studied the properties of P3HT:TiO2 nanocomposite films and the performance of the P3HT:TiO2 nanocomposite solar cells as a function of TiO2 concentration and the solvent used for the film preparation. While significant quenching of the P3HT emission is obtained for all nanoparticle concentrations, the performance of cells with low (<40%) and high (>70%) TiO2 concentration is comparable to or worse than that of cells with pure P3HT. This was attributed to the recombination of the separated charges for lower nanoparticle concentrations and poor film quality for higher nanoparticle concentrations. For 50% and 60% TiO2 concentrations, however, significant improvements are obtained. We also found that the PL quenching and the cell performance exhibit strong dependence on the solvent used, which was attributed to differences in the film morphology, i.e. differences in the degree of mixing between P3HT and TiO2. The best performance was obtained for the cell with 60% TiO2 fabricated from xylene solution, with AM1 power conversion efficiency of 0.42% and EQE reaching 15%.

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