Nanostructured metal oxide/conjugated polymer hybrid solar cells by low temperature solution processes

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Received 9th July 2007, Accepted 22nd August 2007
First published as an Advance Article on the web 7th September 2007
DOI: 10.1039/b710400f

In this article, we have proposed a nanostructured photovoltaic device based on the ZnO nanostructures/poly(3-hexylthiophene)(P3HT):TiO₂ nanorod hybrid by solution processes at low temperature. An array of ZnO nanorods with a larger size of ~50 nm in diameter and ~180 nm in length are grown to provide direct pathways for efficient charge collection. TiO₂ nanorods with a size of ~5 nm in diameter and ~20–30 nm in length are incorporated into polymers to facilitate charge separation and transport by providing an increased interfacial area and a more effective transport pathway. The device performance with the inclusion of TiO₂ nanorods exhibits a seven times increase in the short circuit current with respect to that without TiO₂ nanorods. The device performance can be further enhanced after completely removing the residual surfactant on the TiO₂ nanorods using the ligand exchange method, giving a short circuit current density of 2.67 mA cm⁻² and a power conversion efficiency of 0.59% under Air Mass 1.5 (100 mW cm⁻²) illumination.

Introduction

Recently, dye-sensitized solar cells based on nanoporous TiO₂ thin films can reach an efficiency as high as 10%.¹ However, the requirement of using liquid electrolytes in dye-sensitized solar cells is still a very challenging issue to be resolved for commercial applications. Considerable research has been focused on developing solid state dye-sensitized solar cells or alternatively, polymer solar cells. Polymer solar cells have attracted a great deal of interest recently due to their potential application in developing low-cost, large-area, mechanically flexible photovoltaic devices.²,³ A basic requirement for a photovoltaic material is to generate free charge carriers produced by photoexcitation. Subsequently, these carriers are transported through the device to the electrodes without recombining with oppositely charged carriers. Due to the low dielectric constant of organic materials, the dominant photo-generated species in most conjugated polymers is a neutral bound electron–hole pair (exciton). These neutral excitons can be dissociated from Coulomb attraction by offering an energetically favorable pathway for the electron from the polymer (donor) to transfer onto an electron-accepting species (acceptor). Because the diffusion length of excitons in a semiconducting polymer is usually shorter than 20 nm,⁴,⁵ the electron acceptor must be intermixed with polymer at a nanometre length scale to achieve efficient charge separation. The most commonly used structure is the polymer-based bulk heterojunction (BHJ) solar cell, which consists of an electron-accepting network formed randomly within the polymer matrix. The most popular electron acceptors in BHJ polymer photovoltaic devices are C₆₀ derivatives⁷,⁸ and nanocrystals such as CdSe²⁻⁻ or TiO₂¹⁰⁻¹² or ZnO.¹³ After charge separation, electrons and holes must be transported to the opposite electrode before back recombination occurs. Carrier transport in the BHJ photovoltaic devices is usually limited by the poorly formed electron conducting pathway through hopping. A promising photovoltaic device structure consisting of a direct and ordered path for photogenerated electrons to the collecting electrode has been proposed. This can be done by using templated porous nanostructures,¹⁴⁻¹⁷ or vertically oriented nanorods.¹⁸⁻²⁰ A maximum external quantum efficiency of ~10% has been achieved by filling polymer into well-controlled TiO₂ nanopores synthesized using block copolymers as the structure directing agent.¹⁴ However, the infiltration of polymer into the small TiO₂ nanopores is still not a trivial task. Recently, ZnO nanorods grown perpendicularly to the substrate have attracted a great interest since they can be synthesized through simple processes from solution at low temperature. Photovoltaic devices based on conjugated polymer deposited onto ZnO nanorods¹⁹ or nanofibers²⁰ have been demonstrated recently. Although the optimized structural dimension of less than 20 nm between nanorods is desirable, it is still very challenging to control the precise spacing between ZnO nanorods for infiltrating polymer. In ref. 19, an amphiphilic molecular dye interface between ZnO nanorods and the polymer is therefore required to assist charge separation due to the large film pore sizes (~100 nm) between nanorods. In this article, we propose a nanostructured photovoltaic device based on the ZnO/P3HT:TiO₂ hybrid material as shown in Fig. 1 schematically. Thicker ZnO nanorod arrays are grown on the electrode surface to provide a direct pathway for efficient electron collection. The thinner TiO₂ nanorods are then incorporated into polymer to provide larger interfacial areas and more effective conduction

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paths for charge separation and transport respectively. The mechanisms of efficient charge separation and transport in ZnO/P3HT:TiO$_2$ nanostructured photovoltaic devices have further been investigated by time-resolved photoluminescence (TRPL) spectroscopy and fast transient photocurrent measurements. Considerable improvement in the device performance can be achieved in the nanostructured hybrid photovoltaic device by infiltrating the P3HT:TiO$_2$ hybrid material with respect to that obtained by infiltrating the polymer only.

Material preparation and experimental setup

(1) TiO$_2$ nanorods

The growth of high aspect ratio anatase titanium dioxide nanorods was achieved by the hydrolysis of titanium tetraisopropoxide according to literature methods.$^{21,22}$ Typically, oleic acid (120 g, Aldrich, 90%) was stirred vigorously at 120 °C for 1 h in a three-neck flask under Ar flow, then allowed to cool to 90 °C and maintained at this temperature. Titanium isopropoxide (17 mmole, Aldrich, 99.999%) was then added to the flask. After stirring for 5 min, trimethylamine-$N$-oxide dihydrate (34 mmole, ACROS, 98%) in 17 ml water was rapidly injected. The trimethylamine-$N$-oxide dihydrate was used as a catalyst for polycondensation. The reaction was continued for 10 h to have complete hydrolysis and crystallization. Finally, the TiO$_2$ nanorods were collected by centrifugation and then redispersed in chloroform. Fig. 2(a) shows the X-ray diffraction (XRD) pattern of TiO$_2$ nanorods [Philips PW3040 with filtered Cu K$_\alpha$ radiation ($\lambda = 1.541$ Å)], indicating the formation of the anatase phase. A sharp peak intensity and narrow width of (004) imply the formation of nanorods. The TiO$_2$ nanorod microstructure was measured by a JEOL-2000FX (Japan) transmission electron microscope (TEM) operated at 200 keV. The TEM image of TiO$_2$ nanorods in the inset of Fig. 2(a) reveals that the dimensions of the TiO$_2$ nanorods are 20–30 nm in length and 4–5 nm in diameter. The high-resolution TEM (HRTEM) image of the TiO$_2$ nanorods is shown in Fig. 2(b). The corresponding selected-area diffraction pattern (SADP) of the TiO$_2$ nanorods is also shown in the inset of Fig. 2(b). The d-spacing of this ring pattern is 3.54 Å, 2.39 Å, 1.90 Å and 1.69 Å from inner ring to outer ring. It can be indexed for (101), (004), (200) and (211) of the TiO$_2$ anatase phase, consistent with the XRD result. The filtered image from the square region is also shown, which indicates the growth direction of the TiO$_2$ nanorods is along the longitudinal [001] direction in the synthesized condition. In the preparation of hybrid materials, the P3HT solution was prepared by dissolving P3HT (Aldrich, USA) in chloroform at a concentration of 1 wt%. The hybrid materials were prepared by adding the appropriate amount of TiO$_2$ nanorods to a 1 wt% polymer solution to make composite samples with a ratio of 1 : 1.

(2) Preparation of ZnO nanorods

ZnO nanorod arrays were grown on Au-coated ITO substrates using a pulsed current electrolysis method. Au layers with a thickness of ~10 nm were pre-deposited on the ITO substrates using DC sputtering. The substrate, a platinum wire and an Ag/AgCl electrode were utilized as the working, the counter and the reference electrodes, respectively, in an electrochemical system. A 0.0025 M aqueous solution of Zn(NO$_3$)$_2$ was employed to be the electrolyte. A pulsed wave with a pulse length and a pulse period of 0.01 and 0.1 s, respectively, were used for the growth of ZnO nanorods. The pulsed current density was ~2 mA cm$^{-2}$. Fig. 3(a) shows the typical scanning
electron micrograph (SEM) of the ZnO nanorod array formed using a pulsed current electrolysis method at 80 °C. The diameter and the length of the ZnO nanorods are about ~50 nm and ~180 nm, respectively. The average spacing between nanorods is of the order of ~120 nm (estimated from the top view image).

(3) Device fabrication
For photovoltaic device fabrication, a thin active layer consisting of the P3HT:TiO2 nanorod hybrid was deposited onto ZnO nanorods using spin-coating. The sample was then heated at a temperature of 150 °C for 15 min to facilitate the infiltration of the P3HT:TiO2 nanorod hybrid. Fig. 3(b) shows the cross-sectional SEM image of the ZnO nanorods after infiltration of the P3HT:TiO2 nanorod hybrid. The thin active layer with a thickness of 200 nm was used as a light absorbing and hole transporting material. The device was then fabricated by spin-coating a layer of PEDOT:PSS with an effective thickness of 50 nm before thermal evaporation of the Au top electrode. The highly conductive PEDOT:PSS layer is intended to keep the serial resistance low and to reduce surface roughness by filling the voids in the films. The films were then baked in a vacuum oven for 6 h at 120 °C. Vapor deposition of the Au top electrode was then carried out at pressure around 2 × 10⁻⁶ Torr. The corresponding energy levels obtained from the literature¹,¹⁹ for the nanostuctured photovoltaic device based on ZnO/P3HT:TiO2 nanorod hybrid are shown in Fig. 4.

(4) Characterization
UV-Visible absorption spectra were obtained using an Ocean Optics HR-4000 spectrometer. The steady state PL spectra were taken by the FluoroLog® spectrofluorometer (Jobin-Yvon). Time-resolved photoluminescence spectroscopy was performed with a time-correlated single photon counting (TCSPC) spectrometer (Picoquant, Inc.). A pulse laser (375 nm) with an average power of 1 mW operating at 40 MHz with a duration of 70 ps was used for excitation. Current–voltage measurements were obtained using a solar simulator (Oriel Inc.) using the AM 1.5 filter with an irradiation intensity of 100 mW cm⁻². Fast transient photocurrent measurements²³ were performed by a frequency-tripled Nd:YAG pulsed laser (λ = 355 nm and pulse width ~5 ns) and the signals were recorded by a digital oscilloscope (Tetronix TDS5052B). The film thickness was measured by means of the Veeco M6 surface profiler.

Results and discussions
Fig. 5 shows the normalized absorption spectra of pristine P3HT and ZnO/P3HT:TiO2 nanorod hybrid thin films respectively. The pristine P3HT exhibits a broad absorption spectrum ranging from 350 to 650 nm. The enhanced optical density of the absorption spectra below 380 nm in the hybrid mainly results from the contributions of ZnO nanorods and TiO2 nanorods. A slight blueshift of the P3HT band as well as the appearance of a weaker vibronic structure in the hybrid film is mainly attributed to a loss of P3HT polymer-chain stacking after infiltration into ZnO nanorods and mixing with TiO2 nanorods. As shown in Fig. 4, when the polymer is
excited, charge separation occurs at the interface between the polymer and the ZnO (or TiO$_2$) nanorods, giving a charge-separated state with an electron on the ZnO (or TiO$_2$) nanorods and a hole on the polymer. Charge separation efficiency at polymer–inorganic nanocrystal interfaces can be usually revealed through quenching of the photoluminescence (PL) efficiency and shortening of the measured PL lifetime in the polymer.$^9,^{24}$ Four samples consisting of different configurations are taken for investigation. Sample A (P3HT) represents the pristine P3HT thin film deposited on the ITO substrate. Sample B (ZnO/P3HT) and Sample C (ZnO/P3HT:TiO$_2$) represent the composites by spin-coating neat P3HT and P3HT:TiO$_2$ nanorod hybrid thin active layers onto the array of ZnO nanorods respectively. Sample D (ZnO/TiO$_2$/P3HT:TiO$_2$) has a similar configuration to Sample C but is pre-coated with a very thin TiO$_2$ nanorod layer onto ZnO nanorods before the P3HT:TiO$_2$ nanorod hybrid thin active layers onto the array of ZnO nanorods respectively. Sample D (ZnO/TiO$_2$/P3HT:TiO$_2$) has a similar configuration to Sample C but is pre-coated with a very thin TiO$_2$ nanorod layer onto ZnO nanorods before the P3HT:TiO$_2$ nanorod hybrid layer is deposited. The solution concentration of the pre-coated thin TiO$_2$ nanorod layer is about 10 mg ml$^{-1}$. After spin-coating the thin TiO$_2$ nanorod layer, the sample is heat treated at a temperature of 120 $^\circ$C for 5 min to remove the residual solvent. All these samples have a similar thickness of about 200 nm. Fig. 6 shows the PL decay spectroscopy for the four different samples. It is found that the PL lifetime $\tau_B$ (643 ps) for Sample B is shorter than that of the pristine P3HT thin film $\tau_A$ (735 ps), indicating that charge separation occurs at the interfaces between P3HT and the ZnO nanorods by providing a new non-radiative process for photogenerated excitons. As TiO$_2$ nanorods are blended with P3HT, a large number of interfaces between the polymer and the TiO$_2$ nanorods are generated, leading to more efficient charge separation as a result of the shorter PL lifetime $\tau_C$ (509 ps) for Sample C compared to $\tau_B$. For Sample D, the PL decay lifetime $\tau_D$ (361 ps) is even shorter than $\tau_C$ due to the increasing number of interfaces on the surface of the ZnO nanorods by coating a thin TiO$_2$ nanorod layer before infiltrating the active layer. As a result, more efficient exciton dissociation occurs. The role of the thin TiO$_2$ nanorod layer on the ZnO surface can be as follows. Firstly, inserting this layer can create a second interfacial area for exciton dissociation that might increase the charge transfer rate. In addition, an additional TiO$_2$ nanorod thin film on the ZnO surface can also act as a hole-blocking layer to prevent back recombination$^{25}$ and direct contact between the polymer and the ITO electrode.

The photovoltaic performances of the nanostructured devices based on the ZnO nanorods and P3HT:TiO$_2$ nanorod hybrid are then characterized under simulated AM 1.5 illumination as shown in Fig. 7. Three devices with different configurations are fabricated for comparison. Device I (ZnO/P3HT) is based on neat P3HT film deposited onto ZnO nanorods and exhibits a short circuit current density ($J_{sc}$) of 0.30 mA cm$^{-2}$, an open circuit voltage ($V_{oc}$) of 335 mV, a fill factor (FF) of 0.40, and a power conversion efficiency ($\eta$) of 0.04%. The $\eta$ of the device with a neat P3HT film deposited onto ZnO nanorods is similar to that in ref. 19 but is lower compared to that in ref. 20 with a similar configuration. One possible reason for the higher efficiency in ref. 20 may be due

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**Fig. 5** Normalized absorption spectra of pristine P3HT and ZnO/P3HT:TiO$_2$ nanorod hybrid thin films respectively.

**Fig. 6** Time-resolved photoluminescence spectroscopy for the samples consisting of pristine P3HT (Sample A), ZnO nanorods/P3HT (Sample B), ZnO nanorods/P3HT:TiO$_2$ nanorod hybrid (Sample C) and ZnO nanorods/TiO$_2$ nanorods/P3HT:TiO$_2$ nanorod hybrid (Sample D) respectively.

**Fig. 7** Photovoltaic performances of devices with different configurations. Device I: (ZnO/P3HT); Device II: (ZnO/P3HT:TiO$_2$); Device III: (ZnO/TiO$_2$ nanorods/P3HT:TiO$_2$).
to their usage of smaller diameter ZnO nanofibers, which can be infiltrated into more photoactive materials with a higher light harvesting efficiency. Device II has the configuration of ZnO/P3HT:TiO2 nanorod hybrid and exhibits values for $J_{sc}$, $V_{oc}$, FF, and $\eta$ of 1.96 mA cm$^{-2}$, 380 mV, 0.39, and 0.29\% respectively. Over six times increase in $J_{sc}$ with respect to Device I is achieved due to increased charge separation and transport efficiency after the inclusion of TiO2 nanorods in the polymer. Device III has the configuration of ZnO/TiO$_2$/P3HT:TiO$_2$ by pre-coating a thin TiO$_2$ nanorod film onto ZnO nanorods before the infiltration of the P3HT:TiO$_2$ nanorod hybrid. The device shows $J_{sc}$, $V_{oc}$, FF, and $\eta$ performance of 2.20 mA cm$^{-2}$, 400 mV, 0.35, and 0.31\% respectively. The further increase in $J_{sc}$ of Device III compared to that in Device II is attributed to the addition of the thin TiO$_2$ nanorod layer, which prevents electrons from back recombining with holes in P3HT and allows for the photogenerated current to be collected more effectively. Table 1 summarizes the device performance for different configurations. From the photovoltaic performances of the above devices with different configurations, it is found that the inclusion of TiO$_2$ nanorods in the ZnO/P3HT nanostructured hybrid solar cell can improve the device performance by providing increased interfacial area and a more effective transport pathway. In addition, it is suggested that the device performance for the polymer/nanocrystal hybrid solar cells can be further enhanced by completely removing the possible residual surfactant in the hybrid.\footnote{9} We have therefore carried out the process of ligand exchange to remove the residual surfactant oleic acid (OA) through pyridine treatment according to the literature.\footnote{26} The as-synthesized OA end-capped TiO$_2$ nanorods were dispersed in pyridine and left stirring at 70 °C until the solution turned clear. Afterwards, the treated nanocrystals were washed with hexane and isolated by centrifugation, and redispersed in pyridine. Through these procedures, the OA (original surface ligand) was removed and the pyridine of a weak binding ligand was on the surface of TiO$_2$ nanorods, which can be removed through heating. Following the same device fabrication procedures as above, Device IV has a similar configuration to Device III of ZnO/TiO$_2$/P3HT:TiO$_2$ by pyridine treatment and shows a short circuit current density ($\sim$ 3.0 $\mu$s) was found, indicating that effective carrier transport can be achieved through this design of hybrid architecture.

### Table 1

<table>
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<tr>
<th>Device</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>$V_{oc}$/mV</th>
<th>FF</th>
<th>$\eta$ (%)</th>
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<td>335</td>
<td>0.40</td>
<td>0.04</td>
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<tr>
<td>Device II</td>
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<td>0.39</td>
<td>0.29</td>
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<tr>
<td>Device III</td>
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<td>400</td>
<td>0.35</td>
<td>0.31</td>
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<td>Device IV</td>
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<td>490</td>
<td>0.45</td>
<td>0.59</td>
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</table>

![Fig. 8](image_url) Fast transient photocurrent decay for Device I (ZnO/P3HT) and Device III(ZnO/TiO$_2$ nanorods/P3HT:TiO$_2$) respectively.

![Fig. 9](image_url) (a) Photovoltaic performances of the devices before (Device III) and after (Device IV) removing the surfactant (OA) on the TiO$_2$ nanorods by pyridine treatment. Both the devices have the configuration ZnO/TiO$_2$ nanorods/P3HT:TiO$_2$ hybrids. (b) The corresponding external quantum efficiencies (EQE) of Device IV.
(J_{sc}) of 2.67 mA cm^{-2}, an open circuit voltage (V_{oc}) of 490 mV, a fill factor (FF) of 0.45, and a power conversion efficiency $\eta$ of 0.59% as shown in Fig. 9(a), giving an improvement by nearly a factor of two. The corresponding external quantum efficiency (EQE) of Device IV is shown in Fig. 9(b), which has a maximum value of 24% at 510 nm. Complete removal of the residual surfactant at the P3HT/TiO$_2$ nanorod interfaces leads to direct contact between the polymer and the TiO$_2$ nanorods by removing the insulating barrier, leading to a further improvement in charge separation and transport efficiencies. In addition, the increase in the open circuit voltage $V_{oc}$ after pyridine treatment may be attributed to the change in interfacial dipoles, leading to a shift in the band offset at the TiO$_2$–polymer interface.$^{27}$

Conclusion

In summary, we have proposed a type of nanostructured polymer/inorganic metal oxide hybrid photovoltaic device through low temperature solution processes. Thicker nanostructured ZnO nanorods are grown on the electrode surface to provide direct pathways for efficient charge collection. Thinner TiO$_2$ nanorods are incorporated into the polymer to facilitate charge separation and transport by providing increased interfacial area and an effective transport pathway. Considerable improvement in the device performance is achieved by infiltrating the P3HT:TiO$_2$ nanorod hybrid into ZnO nanorod arrays with respect to that without the incorporation of TiO$_2$ nanorods. The device performance can be further enhanced after completely removing the residual surfactant in the P3HT:TiO$_2$ nanorod hybrid after pyridine treatment.

Acknowledgements

This work is supported by National Science Council, Taiwan (Project No. NSC95-2120-M-002-004) and the US Airforce project (AOARD 064-044).

References