Improved performance of polymer/TiO$_2$ nanorod bulk heterojunction photovoltaic devices by interface modification

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In this article, the polymer photovoltaic devices based on the poly(3-hexylthiophene)/TiO$_2$ nanorods hybrid material is present. An enhancement in the device performance can be achieved by removing or replacing the insulating surfactant on the TiO$_2$ nanorod surface with a more conductive ligand, which can play the role to assist charge separation efficiency or also to prevent from back recombination, giving a large improvement in the short circuit current and fill factor. The relatively high power conversion efficiency of 1.7% under simulated AM 1.5 illumination (100 mW/cm^2) can be achieved, providing a route for fabricating low-cost, environmentally friendly polymer photovoltaic devices by all-solution processes. © *2008 American Institute of Physics.*
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Recently, polymer solar cells have attracted a great interest in developing the low-cost, large-area, mechanically flexible photovoltaic devices.[1–3] Due to the short exciton diffusion length in the semiconducting polymer ($<$20 nm),[4–6] the electron acceptors must be intermixed with polymer at a nanometer length scale to achieve efficient charge separation before recombination. The most commonly used structure is the polymer-based bulk heterojunction (BHJ) solar cell, which consists of the electron accepting network formed randomly within the polymer matrix. In the last decade, research has been focused on the development of polymer BHJ photovoltaic devices, using fullerene or fullerene derivatives as acceptors in combination of polymer as donors, and the highest power conversion efficiency is about ~5%.[2,3] An alternative type of hybrid polymer solar cells, based on conjugated polymers combined with *n*-type inorganic nanocrystals, such as CdSe (Refs. 1 and 7) or TiO$_2$, (Refs. 8 and 9) or ZnO,[10] have been proposed due to the advantage of high electron mobility and excellent chemical and physical stability of inorganic semiconductors. Because of the short exciton diffusion length and the relatively low carrier mobility in polymer, the interfaces between the donors (polymer) and acceptors (nanocrystals) play the crucial role in determining the photovoltaic performance.[11] The environmentally friendly and low-cost TiO$_2$ nanocrystal is a promising material for the hybrid organic:inorganic photovoltaic device applications[8,9,12–14] since its surface can be easily modified with many organic molecules,[15] which may influence the charge transfer efficiency at the interface. In this article, we report the improved efficiency of the photovoltaic device based on the poly(3-hexylthiophene)(P3HT)/TiO$_2$ nanorod hybrid material through interface engineering between polymer and TiO$_2$ nanorods.

The growth of high aspect ratio anatase titanium dioxide nanorods was synthesized by the hydrolysis of titanium tetraisopropoxide according to literature with modification.[16] Details and results have been described in an earlier work.[9] The dimensions of TiO$_2$ nanorods are 20–40 nm in length and 4–5 nm in diameter. Typically, the as-synthesized TiO$_2$ nanorods are capped with insulating surfactant of oleic acid (OA) consisting of long alkyl chain, which may act as a potential barrier for charge transfer. Therefore, we carried out the ligand exchange treatment to replace the original oleic acid ligand using two different kinds of ligand molecules of pyridine (PYR) and anthracene-9-carboxylic acid (ACA). Firstly, the as synthesized OA end-capped TiO$_2$ nanorods were washed with ethanol three times to remove the oleic acid. Then, the TiO$_2$ nanorods were dispersed in pyridine and left under stirring at 70 °C until the solution turned clear. 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. Removal of the residual surfactant on the TiO$_2$ nanorod surface in the hybrid material will lead to direct contact between polymer and TiO$_2$ nanorods. To obtain the ACA end-capped TiO$_2$ nanorods, we mixed the ethanol washed bare TiO$_2$ nanorods in combination with the ACA at 6:1 weight ratio, which were then dispersed in pyridine, and left under stirring at 75 °C until the solution turned into clear and yellow color. The ACA capped nanocrystals were then precipitated by hexane and isolated by centrifuging, and redispersed in mixed solvent which contains pyridine, chloroform, and dichloromethane (1:2:2 by volume ratio). The ligand molecule of ACA, which consists of three benzenelike rings and has a large binding energy between carboxylic acid group and TiO$_2$ nanorods, represents a conductive interface between TiO$_2$ nanorods and polymer. The TiO$_2$ nanorods connected with three different kinds of surface ligands are shown schematically in Fig. 1.

The hybrid materials were prepared by adding appropriate amount of TiO$_2$ nanorods into P3HT (M_w~58 000, PDI 1.62, RR 96%) polymer solution to make P3HT/TiO$_2$ nanorod composite samples. For the photovoltaic device fabrication, a 40 nm thick layer of poly(3,4-ethylene-dioxythiophene) poly (styrenesulfonate) (Baytron P 4083) was spin cast onto the indium-tin-oxide substrate, followed by baking at 120 °C for 30 min. The films were moved into a nitrogen-purged glovebox for subsequent depositions. The thin active P3HT:TiO$_2$ nanorod hybrid layer about 120 nm, obtained from a 10 mg/ml solution at 1:1 weight ratio of P3HT to TiO$_2$ in the mixed solvent, was then deposited by

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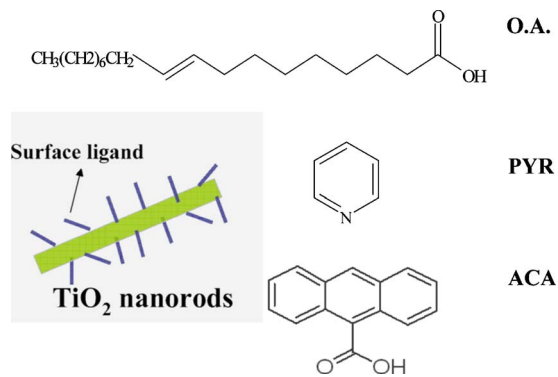b)Electronic mail: suwf@ntu.edu.tw.

FIG. 1. (Color online) Schematic representation of three different kinds of surface ligands on the TiO$_2$ nanorod surface.

using spin coating. An additional layer of TiO$_2$ nanorods sandwiched between the active layer and the aluminum electrode was included to act as a hole blocking layer[9] and also as an optical spacer.[17] Typical device area was about 0.1 cm^2. The Al electrode was then deposited onto the TiO$_2$ nanorod layer by thermal evaporation in vacuum at pressure around 2×10^{-6} Torr.

UV-visible absorption spectra were obtained using Jasco V-570 UV/visible/near-infrared spectrophotometer. The steady state PL spectra were taken by the FluoroLog®-3 spectrofluorometer (Jobin-Yvon). Time-resolved photoluminescence (TRPL) spectroscopy was performed with a time-correlated single photon counting spectrometer (Picoquant, Inc.). A pulse laser (470 nm) with an average power of 1 mW operating at 40 MHz with duration of 70 ps was used for excitation. Current-voltage measurements (Keithley 2410 source meter) were obtained by using a solar simulator (Newport, Inc.) with the AM1.5 filter under irradiation intensity of 100 mW/cm^2. The film thickness was measured by means of the Veeco M6 surface profiler.

The inset in Fig. 2(a) shows absorption spectra of as-

synthesized and ACA-capped TiO$_2$ nanorods, and the two sharp peaks between 350 and 400 nm are related to the fact that the ACA molecules are bonded on the TiO$_2$ nanorods with the carboxylic acid group. Figure 2(a) shows the UV-visible absorption of the hybrid materials with different surface ligand molecules on the TiO$_2$ nanorod surface. The pristine P3HT exhibits a broad absorption spectrum ranged from 400 to 650 nm and TiO$_2$ nanorods have an absorption edge at about 350 nm. The optical density of the absorption spectra in the hybrids is simply the sum of the absorption spectra of constituent parts. For the three samples with different surface treatments, no significant change in the absorption spectra has been found, indicating that the interface layer does not contribute significantly to light harvesting. In contrast, the yield of the PL emission in the three hybrids decreases with different quantities in comparison with the pristine P3HT, as shown in Fig. 2(b), suggesting the occurrence of PL quenching from charge separation. The PL quenching efficiency Q for the three samples is $Q_{ACA} > Q_{PYR} > Q_{OA}$, indicating that more efficient charge separation can be achieved at the P3HT/TiO$_2$ nanorod interfaces by either removing the insulating surfactant or replacing with a more conductive ligand. The improved charge separation efficiency at the P3HT/TiO$_2$ nanorod interfaces can also be inferred from TRPL spectroscopy. Figure 2(c) shows the PL decay curves for the pristine P3HT and the hybrid films with different surface modifications, respectively. The addition of TiO$_2$ nanorods in polymer results in a new relaxation process, which provides a further non radiative process to the donor and leads to shortening of the measured lifetime τ. The measured PL lifetimes for the pristine P3HT and P3HT/TiO$_2$ nanorod hybrids with OA, PYR, and ACA surfactant are $\tau_{P3HT}=676$ ps, $\tau_{OA}=480$ ps, $\tau_{PYR}=310$ ps, and $\tau_{ACA}=291$ ps, respectively, indicating that more efficient charge separation takes place at the polymer/TiO$_2$ nanorod interfaces by removing the insulating ligand OA or by re-
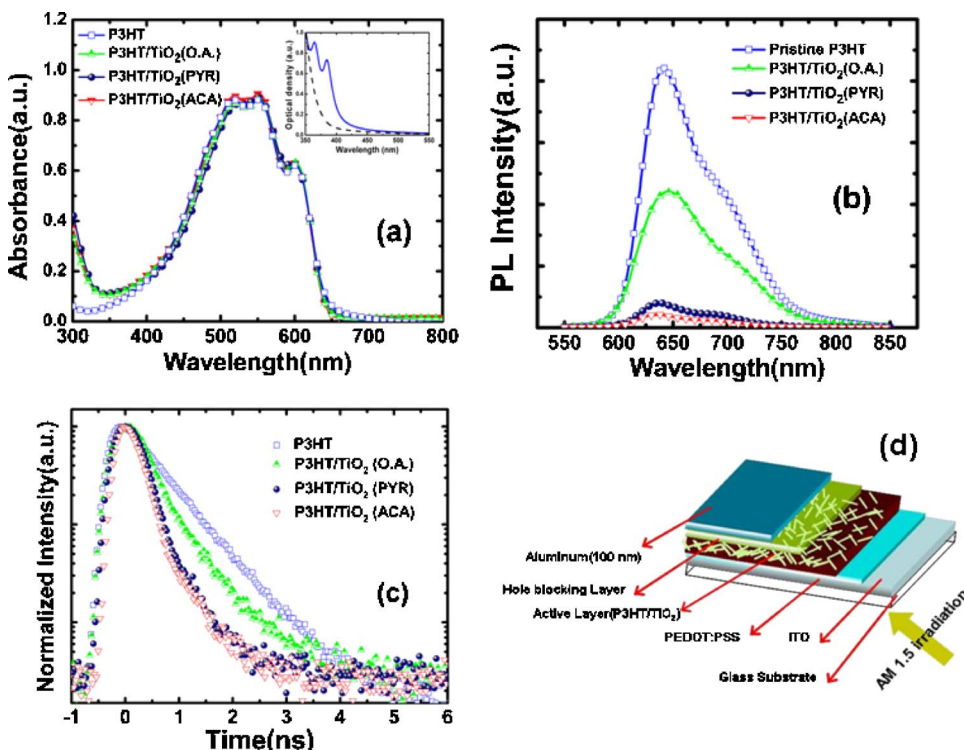

FIG. 2. (Color online) (a) UV-visible absorption, (b) PL intensity, and (c) time-resolved PL spectroscopy of the hybrid materials with different surface ligand molecules. The inset in (a) shows absorption spectra of as-synthesized (dash line) and ACA capped TiO$_2$ nanorods (solid line). (d) Schematic representation of the photovoltaic device based on the hybrid material.
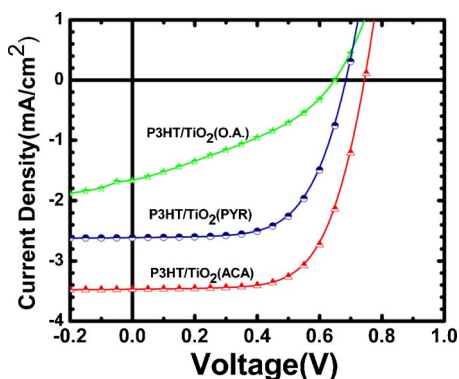
FIG. 3. (Color online) Current-voltage characteristics of the photovoltaic devices based on different surface ligand molecules under AM 15 (100 mW/cm^2) irradiation.

placing with a more conductive ligand of ACA, consistent with the PL quenching result.

We have further fabricated the photovoltaic devices using the above three hybrid materials, as shown schematically in Fig. 2(d). All the devices consisting of different surface modified TiO$_2$ nanorods were fabricated using the same P3HT:TiO$_2$ nanorod ratio of 50:50 wt %. The current-voltage characteristics of the devices with different configurations under simulated AM 1.5 illumination are shown in Fig. 3. The device based on the P3HT:TiO$_2$ nanorod (OA) hybrid material exhibits a short circuit current density (J_{sc}) of 1.67 mA/cm^2, an open circuit voltage (V_{oc}) of 0.65 V, and a fill factor (FF) of 0.35, resulting in a power conversion efficiency (η) of 0.38%. For the device based on the hybrid with TiO$_2$ nanorods by pyridine treatment, a large increase in the fill factor indicates that removal of insulating surfactant on the TiO$_2$ nanorods results in a significant improvement in the serial resistance of the device. The performance of the device based on the P3HT:TiO$_2$ nanorod (PYR) hybrid material exhibits a short circuit current density (J_{sc}) of 2.62 mA/cm^2, an open circuit voltage (V_{oc}) of 0.69 V, and a FF of 0.63, resulting in a power conversion efficiency (η) of 1.14%. For the device consisting of TiO$_2$ nanorods modified by the conductive ligand of ACA, a further improvement in the device performance is found, giving a short circuit current density (J_{sc}) of 3.49 mA/cm^2, an open circuit voltage (V_{oc}) of 0.75 V, and a FF of 0.65, resulting in a power conversion efficiency (η) of 1.7%. Table I summarizes the device performance for different configurations. The role of the conductive surface ligand molecule ACA may act as follows: (i) it can mediate charge transfer from the polymer to the TiO$_2$ nanorods for electron accepting and result in a more efficient charge separation, similar to the observation in Ref. 15 for the polymer/TiO$_2$ interface. However, the exact

nature of charge transfer efficiency could differ in the hybrid compared to a monolayer on a flat surface. (ii) The molecular structure of ACA consisting of anthracene may also interact with the thiophene rings of P3HT, which may further improve the compatibility between polymer and TiO$_2$ nanorods. (iii) The surface modifier may also act as a barrier from back recombination, which can reduce the shunt losses and improve the device performance.[18,19] (iv) The surface traps or defects of TiO$_2$ nanorods can also be modified by the interface modifier, which can assist the charge transfer efficiency. The detailed origin is now under investigation. The relatively high power conversion efficiency of the P3HT/TiO$_2$ nanorod hybrid solar cells provides a route for future application of fabricating low-cost, environmentally friendly photovoltaic devices by all-solution processes.

In summary, we have demonstrated the polymer photovoltaic devices based on P3HT/TiO$_2$ nanorod hybrid material. The performance of the solar cell can be significantly improved through interface modification. Further optimization in the device performance can be accomplished by varying the size of nanorods, improving the polymer/nanorod interface, or aligning the nanorods to improve the carrier transport.

TABLE I. Summary of the device performance based on P3HT/TiO$_2$ nanorod hybrid materials with different surface modifications.

	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
P3HT/TiO$_2$ (OA)	1.67	0.65	0.35	0.38
P3HT/TiO$_2$ (PYR)	2.62	0.69	0.63	1.14
P3HT/TiO$_2$ (ACA)	3.49	0.75	0.65	1.70

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