Balanced Dipole Effects on Interfacial Engineering for Polymer/TiO₂ Array Hybrid Solar Cells

Fan Wu 1*, Yanyan Zhu 1, Xunheng Ye 1, Xiaoyi Li 1, Yanhua Tong 2 and Jiaxing Xu 1

Abstract

The polymer/TiO₂ array heterojunction interfacial characteristics can be tailored by balanced dipole effects through integration of TiO₂-quantum dots (QDs) and N719 at heterojunction interface, resulting in the tunable photovoltaic performance. The changes of \( V_{oc} \) with interfacial engineering originate from the shift of the conduction band \( (E_c) \) edge in the TiO₂ nanorod by the interfacial dipole with different directions (directed away or toward the TiO₂ nanorod). The \( J_{sc} \) improvement originates from the enhanced charge separation efficiency with an improved electronic coupling property and better charge transfer property. The balanced dipole effects caused by TiO₂-QDs and N719 modification on the device \( V_{oc} \) are confirmed by the changed built-in voltage \( V_{bi} \) and reverse saturation current density \( J_{sc} \).

Keywords: TiO₂, Array, Hybrid solar cells, Interfacial engineering

Background

TiO₂ is mainly used in photocatalytic and photoelectrode for photocurrent because of its nontoxicity, high electron mobility, and high chemical and thermal stability [1, 2]. Hybrid solar cells (HSCs) based on conjugated conducting polymers (donor) and TiO₂ nanocrystals (acceptor) have received extensive attention, as they have the potential to offer low-cost, mechanically flexible, and up-scalable alternatives to conventional photovoltaics [3, 4]. A promising photovoltaic device structure for HSC consisting of a direct and ordered path, instead of disordered three-dimensional networks of interconnected nanoparticles for electron transport to the collecting electrode, has been proposed [5, 6]. Single-crystalline rutile TiO₂ nanorod arrays (NRAs) are hydrothermally grown directly on fluorine-doped tin oxide (FTO) substrates as acceptors to dissociate excitons and collect electrons in a HSC, which demonstrates an enhanced power conversion efficiency compared with that of the dense TiO₂ film-based device [7, 8]. However, in general, the polymer/pristine TiO₂-NRA solar cells perform poorly, wherein most of the open-circuit voltage \( (V_{oc}) \) is 0.30–0.44 V and the short-circuit current \( (J_{sc}) \) is between 0.28–2.20 mA/cm² [7–10]. It was demonstrated that the interfaces between the polymer and the nanocrystals play a crucial role in determining the photovoltaic performance. The relatively poor performance of the polymer/pristine TiO₂-NRA solar cells can be partly attributed to the undesirable interfacial properties between the polymer and TiO₂-NRAs [11, 12].

Optimization of the polymer/nanocrystal interface can enhance the charge separation efficiency and reduce the charge recombination and is an important issue for efficient HSC devices [13]. Therefore, to improve device performance, various studies have been performed on modified TiO₂-NRA surfaces. For example, TiO₂-NRA modified with an organic molecule (i.e., D149) has improved the \( J_{sc} \) to 3.93 mA/cm² and \( V_{oc} \) to 0.60 V due to the improved compatibility of the interface morphology [11]; inorganic modification of TiO₂-NRA, such as with crystalline CdS-quantum dots (QDs), normally results in an increase in \( J_{sc} \) to 1.51 mA/cm² and \( V_{oc} \) of 0.45 V [7]; and modification with crystalline CdSe-QDs normally results in an increase in \( J_{sc} \) to 1.15 mA/cm² and \( V_{oc} \) of 0.62 V [14]. It is obvious that both the organic and inorganic modifications differentially affect the polymer/TiO₂-NRA devices’ performance. At present, few studies on interfacial engineering of combinations of the organic
and inorganic material in the polymer/TiO$_2$-NRA HSCs have been reported. Zhang et al. studied the composite interfacial modification in the P3HT/TiO$_2$-NRA interface using inorganic (CdSe) and organic (N719 dye, pyridine) materials as modifiers [15]. At present, there are some limitations to improve the device performance by the method of monomodification, which leads to the moderate improvement in device efficiency. In their results, the performance of composite interfacial modification was superior to that of modifications based on a monolayer. Obviously, engineering the heterojunction interface using organic and inorganic materials simultaneously in polymer/TiO$_2$-NRA HSCs is a method for further improving the photovoltaic performance.

This work aims at the heterojunction interface of polymer/TiO$_2$-NRA HSCs, two functional materials of TiO$_2$-QDs and N719 dyes are constructed at the interface of polymer/TiO$_2$-NRA with certain principles as depicted in Fig. 1, which generates the synergistic effects on device performance. Results showed that the efficiency in our polymer/TiO$_2$-NRA solar cells can be improved nearly fourfold by engineering the heterojunction interface. Moreover, the photovoltaic performance can be tailored through different amounts of TiO$_2$-QDs and N719 at heterojunction interface, resulting in the tunable photovoltaic performance.

**Methods**

**Synthesis of TiO$_2$-NRA**

TiO$_2$-NRA was hydrothermally grown on FTO-coated glass (14 $\Omega$/sq, 400 nm FTO thickness, Nippon Sheet Glass Co.) according to the reported procedure [16]. Deionized water (30 mL) was mixed with 30 mL of concentrated hydrochloric acid (35%) to reach a total volume of 60 mL in a Teflon-lined stainless steel autoclave (100 mL volume). The mixture was stirred in ambient conditions for 5 min, the cleaned FTO substrate was put upside down in the Teflon liner, and 1 mL of titanium (IV) isopropoxide was added. After 10 min of ultrasonic solving, the autoclave was sealed and autoclaving was conducted at 180 °C for 2 h in an electric oven to produce TiO$_2$-NRA.

**Synthesis of TiO$_2$-NRA@TiO$_2$-QDs**

The TiO$_2$-NRA substrate was removed, rinsed extensively with deionized water, and dried under airflow. Subsequently, the TiO$_2$-NRA substrate was put upside down in the Teflon liner and added 0.1 M titanium isopropoxide ethanol solution. The sealed autoclave was heated to 200 °C in an electric oven for another 4 h to produce TiO$_2$-CSA. Once it cooled, the substrate was removed and dried under airflow after carefully rinsing it with anhydrous alcohol several times.

**Synthesis of TiO$_2$-NRA@TiO$_2$-QDs@N719**

The dried TiO$_2$-NRA@TiO$_2$-QD substrate was immersed in ethanol solution of N719 (5 x 10$^{-6}$ M) in an autoclave and heated to 80 °C for 8 h in an electric oven. After the autoclave was cooled to room temperature, the substrate was removed and rinsed with alcohol several times to remove the excess dye, providing the sample TiO$_2$-NRA@TiO$_2$-QDs@N719.

**Device Fabrication**

The procedure used for fabrication of solar cells was similar to that described in previous works [17, 18]. Poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) (average Mn = 40000 – 70000, Aldrich) and poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) (Clevios P HC V4, H. C. Starck) were commercially obtained. The MEH-PPV layer was deposited on the top of the array by spin-coating (1500 rpm, 40 s) the MEH-PPV solution in chlorobenzene (10 mg/mL) under ambient conditions. Active layer deposition was followed by annealing at 150 °C under N$_2$ atmosphere for 10 min. Subsequently, a PEDOT:PSS film was spun coated (2000 rpm, 60 s) over the polymer layer. After the deposition of PEDOT:PSS, the sample was sequentially heated for 10 min at 100 °C in a N2 glove box. Finally, a gold electrode (100 nm) was evaporated through a shadow mask to form an overlapped area of 3 mm × 3 mm between the indium tin oxide (ITO) and Au, which was defined as the effective device area.

![Fig. 1 Schematic illustration for the interfacial engineering in a polymer/TiO$_2$-NRA solar cell by a combination of TiO$_2$-QDs and organic molecules N719 and the architecture of solar cells](image-url)
Scanning electron microscopy (SEM) measurements of nanostructures were performed with field-emission scanning electron microscopy (FE-SEM, Hitachi S-4700). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) studies were performed on a JEOL-2010 microscope under an acceleration voltage of 200 kV. The room temperature photoluminescence (PL) properties were measured in ambient conditions. PL measurements were made with a Hitachi F-7000 spectrofluorophotometer. The steady-state $J-V$ curves were measured with AM 1.5 illumination under ambient conditions using a 94023A Oriel Sol3A solar simulator (Newport Stratford, Inc.) with a 450 W xenon lamp as the light source. Incident photon-to-current efficiency (IPCE) spectra of the solar cells were measured by using a QE/IPCE measurement kit (Zolix Instruments Co., Ltd.) in the spectral range of 300 – 900 nm.

Results and Discussion

Figure 2a shows a typical side view of the SEM image of an as-synthesized TiO$_2$-NRA. The rods stand almost perpendicular to the substrate, have a similar diameter in the 40 to 50 nm range, and are about 500-nm long. The TiO$_2$ nanorods in the array are quite smooth surfaces. The SEM image of the TiO$_2$-NRA after growth of TiO$_2$-QDs (TiO$_2$-NRA@TiO$_2$-QDs) is presented in Fig. 2b. Compared to bare TiO$_2$-NRA, obvious rough grains eventually spanning the entire nanorod can be observed in the side view and top view. The XRD pattern of the NRA@QD sample (Additional file 1: Figure S1) was only indexed to TiO$_2$, which confirms that the rough grains are TiO$_2$. Figure 3 shows a typical TEM image of a sample of TiO$_2$-NRA and TiO$_2$-NRA@TiO$_2$-QDs. The TiO$_2$ nanorod was single crystalline with quite a smooth surface (Fig. 3a). The lattice fringes with interplanar spacings of 0.29 and 0.32 nm match the crystal planes (001) and (110) of rutile TiO$_2$, respectively [16]. Figure 3c shows a typical TEM image of a single rod from the TiO$_2$-NRA@TiO$_2$-QDs. The coarse surface clearly shows that the TiO$_2$ nanorod is covered by a TiO$_2$-QD layer. Figure 3d is a HRTEM image of the rectangular area in Fig. 3c. The shell contains differently oriented TiO$_2$-QDs with 3 - 5 nm grain sizes. The TiO$_2$-NRA@TiO$_2$-QD structures after bonding with (Bu$_4$N)$_2$(Ru)(dcbpyH)$_2$(NCS)$_2$ (called N719) organic molecules were characterized by the absorption spectra and the FT-IR (Additional file 1: Figure S2, in the Supplementary data), which suggest that N719 molecules are chemically grafted onto the TiO$_2$ surface.

HSCs based on TiO$_2$-NRA, TiO$_2$-NRA@TiO$_2$-QDs, and TiO$_2$-NRA@TiO$_2$-QDs@N719 with the conjugated polymer MEH-PPV were fabricated, the architecture of the device is shown in Fig. 1. The illuminated $J-V$ curves (Fig. 4) were measured under the AM 1.5 illumination of 100 mW/cm$^2$ and the photovoltaic parameters were extracted in the Table 1. The MEH-PPV/TiO$_2$-NRA device exhibits a rather low $V_{oc}$ (0.314 V), $J_{sc}$ (2.048 mA/cm$^2$), and efficiency (0.236%) [7–12]. In contrast, after the 4-h growth of the TiO$_2$-QDs on TiO$_2$-NRA to form the NRA@QD structure, the $V_{oc}$ are significantly improved, accompanying little improvement in $J_{sc}$. Further increasing the growth time of TiO$_2$-QDs will lead to a very slight increase in $V_{oc}$ but the $J_{sc}$ decreased because the decreased amount of polymer infiltrated into nanorod interspaces [17, 18]. After modifying the TiO$_2$-NRA@TiO$_2$-QDs (4 h) with N719 by an 4-h solvothermal reaction, a higher $J_{sc}$ of 3.233 mA/cm$^2$ was obtained, which is 2–3 fold higher than that of the MEH-PPV/pristine TiO$_2$-NRA counterpart device; however, the $V_{oc}$ decreased slightly. The power conversion efficiency was enhanced from 0.236 to 0.911%. We also took the N719 reaction time of 8 h to modify the TiO$_2$-NRA@TiO$_2$-QD sample. It was found that the $V_{oc}$ was further decreased, but the $J_{sc}$ (4.222 mA/cm$^2$) was further improved over the sample with the 4-h reaction time. The devices also showed the good stability (Additional file 1: Figure S3, in the Supplementary data). These results suggest that $V_{oc}$ and
$J_{\text{sc}}$ in polymer/TiO$_2$-NRA solar cells can be tuned by engineering their heterojunction interface with the integration of inorganic and organic materials. The mechanism in detail of above phenomenon will be discussed as follows.

It is well known that $V_{\text{oc}}$ in the polymer/inorganic solar cells is mainly determined by the energy levels of the $E_c$ edge in the inorganic material and highest occupied molecular orbital ($E_{\text{HOMO}}$) band in the polymer (Fig. 5a) \[6, 19\]. The larger $V_{\text{oc}}$ in the device with TiO$_2$-NRA@TiO$_2$-QDs than in the device with pristine TiO$_2$-NRA has been demonstrated from the generation of interfacial dipoles in QD shell/polymer interfaces \[17, 18\]. The interfacial dipole generation can be considered as the formation of weakly bound pairs of electrons and holes with separations of a few nanometers by Coulombic attraction \[20\]. These interfacial dipoles commonly arise due to the trapping of electrons at surface states in TiO$_2$-QD shell with a negative charge at the metal oxide surface and positive charge at the polymer (Fig. 5b) \[19\]. The $E_c$ of the TiO$_2$ nanorod can be changed by $\delta E$ with the presence of interfacial dipoles as is similar to the interfacial modification with dipole molecules in P3HT/TiO$_2$ \[21\] and P3HT/ZnO solar cells \[22\], in which $\delta E$ is the change of the surface potential and can be calculated from Poisson’s equation \[23\],

$$\delta E = N \mu \cos \theta / \varepsilon \varepsilon_0$$  \hspace{1cm} (1)

where $N$ is the dipole concentration, $\mu$ the dipole moment, $\theta$ the angle the dipole makes to the TiO$_2$ nanorod surface normal, $\varepsilon_r$ the dielectric constant of TiO$_2$, and $\varepsilon_0$ the permittivity of free space. If dipoles are directed away from the TiO$_2$ nanorod, $\cos \theta > 0$ and leading to $\delta E > 0$; if dipoles are directed toward the TiO$_2$ nanorod, $\cos \theta < 0$, leading to $\delta E < 0$. Therefore, the magnitude of $E_c$ shifting correlates with the dipole concentration and direction in the shell/polymer interface.

### Table 1 Photovoltaic parameters of solar cells under the AM 1.5 illumination of 100 mWcm$^{-2}$

|          | $V_{\text{oc}}$ (V) | $J_{\text{sc}}$ (mA/cm$^2$) | FF (%) | $\eta$ (%) |
|----------|---------------------|-----------------------------|--------|------------|
| NRA      | 0.314               | 2.048                       | 36.740 | 0.236      |
| NRA@QDs (4 h) | 0.695             | 2.450                       | 36.218 | 0.616      |
| NRA@QDs (8 h) | 0.705             | 1.680                       | 37.308 | 0.441      |
| NRA@QDs (4 h)@N719 (4 h) | 0.630          | 3.233                       | 40.980 | 0.834      |
| NRA@QDs (4 h)@N719 (8 h) | 0.540          | 4.222                       | 39.956 | 0.911      |
presence of dipoles directed away from the TiO$_2$ in the shell/polymer interface (i.e., $\cos \theta > 0$) due to the TiO$_2$-QD shell (Fig. 8b), the $E_c$ of the TiO$_2$ nanorod core will be shifted toward the local vacuum level of the polymer due to the $\delta E > 0$ (Fig. 5b).

The obtained $V_{oc}$ of 0.54 and 0.63 V for the MEH-PPV/TiO$_2$-NRA@TiO$_2$-QDs&N719-based device, however, are somewhat lower than the value of 0.69 V for the MEH-PPV/TiO$_2$-NRA@TiO$_2$-QD-based counterpart device. This results from the modification of the ZnO surface by N719, stemming from the dissociative adsorption of the carboxylic acid group to form a carboxylate bond, in which the positive proton charge on the surface and the negative charge on the carboxylic group together form an interfacial dipole [21, 22]. A theoretical calculation has demonstrated the direction of the dipoles generated by the adsorbed N719 molecules on the oxide surface with the monodentate anchoring mode directed to the oxide surface (i.e., $\cos \theta < 0$) (Fig. 5b) [22]. In this case, the dipole concentration generated by the modification with N719 will change the $E_c$ of the TiO$_2$ nanorod with $\delta E < 0$ based on eq. (1). That means the $V_{oc}$ will be reduced by the band edge potential of TiO$_2$ closer to the polymer $E_{vac}$ [20, 24]. The $V_{oc}$ in the MEH-PPV/TiO$_2$-NRA@TiO$_2$-QDs&N719 device with 8 h of N719 bonding time was further confirmed in this conclusion (Fig. 2 and Table 1). The dipole concentration in the sample MEH-PPV/TiO$_2$-NRA@TiO$_2$-QDs&N719 with 4 h of N719 bonding time should be lower than the 8-h sample based on eq. (1), which causes the $V_{oc}$ in the 8-h device MEH-PPV/TiO$_2$-NRA@TiO$_2$-QDs&N719 to be lower than MEH-PPV/TiO$_2$-NRA@TiO$_2$-QD&N719 with 4 h. Therefore, there is a balance of dipole effects (i.e., positive or negative of $\delta E$ and its magnitude) by QD layer and N719 modification on device $V_{oc}$.

In addition, the interfacial dipoles were confirmed by the changed built-in voltage $V_{bi}$ (Fig. 6) and reverse current $J_s$ (Fig. 7). The $V_{bi}$ related to built-in electric field ($E_{bi}$) which originates the work-function difference between the ITO and Au electrodes could be observed at the point where the dark $J−V$ curve begins to follow quadratic behavior [25]. The interfacial dipoles (directed toward the polymer) could induce an extra polar electric field to enhance $E_{bi}$, which is confirmed by the enhanced $V_{bi}$ in Fig. 6a [22, 23]. Moreover, the $E_c$ edge shifts in the TiO$_2$ nanorod due to the number of dipole formations also agree with the changes of the reverse saturation current density $J_s$ in the devices, which aroused our much interest. It has been demonstrated that there is often an interface activation energy barrier $\Phi_B$ at the heterojunction, which is usually explained as a result of the energy level bending by the vacuum level misalignments at the heterojunction, and could be affected by formation of interface charge transfer state or dipoles [26, 27]; the $\Phi_B$ can be evaluated from the dark reverse saturation current in dark $J−V$ characteristic by [40,41]

$$J_s = A \exp \left( -\frac{\Phi_B}{nkT} \right)$$

where $A$ is a coefficient with a value in the vicinity of 1000 A/cm$^2$ for the reverse bias current generation, and $k$ and $T$ are the Boltzmann constant and temperature, respectively.
The current density–voltage of solar cells in the dark can be described by the following modified ideal diode equation [28]:

\[
J_d = J_s \left( \exp \left( \frac{q(V - J_d R_s)}{n k T} \right) - 1 \right)
\]

(3)

where \(J_s\) is reverse saturation current density, \(q\) elementary charge, \(V\) applied voltage, \(R_s\) device series resistance, \(n\) diode ideality factor, \(k\) Boltzmann’s constant, and \(T\) temperature. We note that \(V >> J_d R_s\) for our devices, since \(J_d\) generally less than 0.01 A/cm², and \(R_s\) is generally less than 200 Ω/cm². Neglecting the \(J_d R_s\) term in eq. (1), for \(V \geq \frac{n k T}{q}\), we can get the following relation:

\[
\ln J_d = \ln J_s + \frac{q}{n k T} V
\]

(4)

Equation (4) indicates that a plot of \(\ln J_d\) versus \(V\) should yield a straight line. Therefore, \(J_s\) and \(n\) can be extracted from the \(\ln J_d - V\) curves in the linear region, which \(q/n k T\) and \(\ln J_s\) corresponds to the slope and \(y\)-intercept, respectively (Fig. 8). Therefore, we extracted the approximate value of dark reverse saturation current \(J_s\) from the dark \(J - V\) curve based on eq. 4 [29].

Based on eq. 2, we calculated the interface energy barrier \(\Phi_B\) values of all devices (Fig.7b). The energy barrier \(\Phi\) for this process is correlated, but not necessarily just equal, to the difference between the \(E_c\) and \(E_{HOMO}(E_c - E_{HOMO}\) in Fig. 7a) due to the complicated interfacial dynamic processes [28, 30]. If there was a shift of the \(E_c\) edge in the TiO2 nanorod, it would affect the \(E_c - E_{HOMO}\) (i.e., \(\Phi\)), and thereby influence the \(J_s\) based on eq. 2. The changes of device \(J_s\) and \(V_{oc}\) with interfacial engineering are depicted in Fig. 7b. It is observed that \(J_s\) decreased from \(2.76 \times 10^{-3}\) mA/cm² in the MEH-PPV/TiO2-NRA device to \(2.03 \times\)
$10^{-4}$ mA/cm$^2$ in the MEH-PPV/TiO$_2$-NRA@TiO$_2$-QD device; therefore, the energy barrier $\phi$ (or $E_c-E_{\text{Homo}}$) increased based on eq. 2, which agrees with the expectation on the up-shift of the $E_c$ edge in the TiO$_2$ nanorod after the growth of the QD layer in Fig. 5b. Additionally, the little increase of $J_s$ ($3.35 \times 10^{-4}$ mA/cm$^2$) after the engineering of N719 agrees with the small downshift of the $E_c$ edge in the TiO$_2$ nanorod (i.e., $\phi$) due to the adsorbed N719 molecules on the TiO$_2$-QD surface with monodentate anchoring mode directed to the TiO$_2$ surface in Fig. 5b.

The improved $J_{sc}$ in device performance after the interface modification was studied by IPCE and PL spectra (Fig. 9). The slightly enhanced IPCE (or $J_{sc}$) in the MEH-PPV/TiO$_2$-NRA@TiO$_2$-QD device resulted from the small increase of the interfacial area due to the formation of the coarse shell for exciton dissociation in comparison to the smooth surface of the original TiO$_2$ nanorods. However, the largely improved $J_{sc}$ by modification of the TiO$_2$-NRA@TiO$_2$-QDs with N719 originates from the enhanced charge separation efficiency [22]. The amphiphilic dye improved the interface contact between the polymer and TiO$_2$-NRA@TiO$_2$-QDs, which improves the electronic coupling property for charge transfer. These explanations agree with the PL quenching results (Fig. 9b). Obviously, the PL intensity of the MEH-PPV/TiO$_2$-NRA composite decreases significantly as compared with the intensity of pristine MEH-PPV, indicating that the PL emission of MEH-PPV can be quenched by TiO$_2$ nanorods resulting from the electron transfer from MEH-PPV to TiO$_2$ [31]. After engineering the TiO$_2$-NRA surface with TiO$_2$-QDs and TiO$_2$-QDs@N719, the degree of PL quenching become more obviously, especially in the MEH-PPV/TiO$_2$-NRA@TiO$_2$-QDs@N719 sample. The
PL quenching and IPCE (or $J_{sc}$) follow similar trends indicating that the increased photocurrent upon the MEH-PPV/TiO$_2$-NRA@TiO$_2$-QDs@N719 indeed originates from the better charge separation and transfer at the heterojunction interface.

Conclusions

The heterojunction interfacial engineering in polymer/TiO$_2$ nanorod array (NRA) hybrid solar cells was performed in two steps: first, we grew TiO$_2$-quantum dots (QDs) on a TiO$_2$-NRA surface to form the TiO$_2$-NRA@TiO$_2$-QD structure. Next, the TiO$_2$-NRA@TiO$_2$-QD structure was further bonded with organic molecules (N719) on its surfaces to form the TiO$_2$-NRA@TiO$_2$-QDs@N719 composite array through the solvothermal method. By controlling the interfacial engineering for polymer/TiO$_2$-NRA solar cells through the integration of TiO$_2$-QDs and N719 molecules, the $V_{oc}$ and $J_{sc}$ in polymer/TiO$_2$-NRA@TiO$_2$-QDs@N719 solar cells can be tuned, improving the device efficiency nearly four times compared with that of pristine TiO$_2$-NRA-based solar cells. The tunable device performance is resulted from the balanced interfacial dipoles, which is confirmed by the changed built-in voltage $V_{bi}$ and reverse current $J_{rev}$. These results therefore provide information crucial to the optimization of interface in HSCs.

Additional file

Additional file 1: Supplementary Data. Figure S1. XRD of TiO$_2$-NRA and TiO$_2$-NRA@TiO$_2$-QDs on the FTO substrate. Figure S2. (a) UV-vis absorption spectra of TiO$_2$-NRA (c), TiO$_2$-NRA@TiO$_2$-QDs (c), and TiO$_2$-NRA@TiO$_2$-QDs@N719 (+). The inset in (a) is the absorption spectra of N719 in the ethanol solution; (b) FT-IR spectra of TiO$_2$-NRA@TiO$_2$-QDs (1), TiO$_2$-NRA@TiO$_2$-QDs@N719 (2), and N719 (3). Figure S3. The $J$–$V$ performance of fresh device and measured after 60 days. (DOC 4431 kb)

Acknowledgements

We acknowledge the “1112 Talents Project” of Huzhou City and the valuable suggestions from the peer reviewers.

Funding

The role of the National Natural Science Foundation of China (21607041; 11547312; 11647306) is designing the work; the role of the Science and Technology Planning Project of Zhejiang Province (2017C33240), Seed Fund of Young Scientists Research Talents of Huzhou University (RK21056), and Foundation of Science and Technology Innovation Activities & Emerging Talents Plan of Zhejiang Province (2015R427005; 2016R42707) is the collection, analysis, and interpretation of the data.

Authors’ Contributions

FW carried out the experiments and drafted the manuscript. YZ, XY, and JX participated in the device preparation. XL participated in the design of the study. YT conceived of the study and helped to draft the manuscript. All authors read and approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

Author details

1School of Science and Key Lab of Optoelectronic Materials and Devices, Huzhou University, Huzhou 313000, People’s Republic of China. 2Department of Material Chemistry, Huzhou University, Huzhou 313000, People’s Republic of China.

Received: 12 October 2016 Accepted: 28 January 2017
Published online: 03 February 2017

References

1. Zheng L, Han S, Liu H, Yu P, Fang X (2016) Hierarchical MoS$_2$ nanosheets/TiO$_2$ nanotube array composites with enhanced photocatalytic and photocurrent performances. Small 12:1527–1536
2. Iandolo B, Wickman B, Svensson E, Paulsson D, Hellman A (2016) Tailoring charge recombination in photoelectrodes using oxide nanostructures. Nano Lett 16:2381–2386
3. Chiang C, Lee Y, Lee Y, Lin G, Yang M, Wang L, Hsieh C, Dai C (2016) One-step in situ hydrothermal fabrication of D/A poly(3-hexylthiophene)/TiO$_2$ hybridnanowires and its application in photovoltaic devices. J Mater Chem A 4:908–919
4. Armstrong CL, Price MB, Munoz-Rojas D, Davis NJKL, Abdi-Jalebi M, Friend RH, Greenham NC, MacManus-Driscoll JL, Böhm ML, Musselman KP (2015) Influence of an inorganic inter layer on exciton separation in hybrid solar cells. ACS Nano 9:11863–11871
5. Yu M, Long Y, Sun B, Fan Z (2012) Recent advances in solar cells based on one-dimensional nanostructure arrays. Nanoscale 4:2783–2796
6. Xu T, Qiao Q (2011) Conjugated polymer-inorganic semiconductor hybrid solar cells. Energy Environ Sci 4:2700
7. Xie YL (2013) Enhanced photovoltaic performance of hybrid solar cell using highly ordered CdS/CdSe-modified TiO$_2$ nanorods. Electrochim Acta 105:137–141
8. Zhang Q, Yodyingyong S, Xi J, Myers D, Cao G (2012) Oxide nanowires for solar cell applications. Nanoscale 4:1436–1445
9. Liao W, Hsu S, Lin W, Wu J (2012) Hierarchical TiO$_2$ nanostructured array/ P3HT hybrid solar cells with interfacial modification. J Phys Chem C 116:15938–15945
10. Baeten L, Conings B, De Smet S (2012) Fully water-processable metal oxide nanorods/polymer hybrid solar cells. Sol Energy Mater Sol Cells 107:230–235
11. Hsu S, Liao W, Lin W, Wu J (2012) Modulation of photocarrier dynamics in indoline dye-modified TiO$_2$ nanorod array/P3HT hybrid solar cell with 4-tert-butylpyridine. J Phys Chem C 116:25721–25726
12. Liao W, Wu J (2013) Efficient electron collection in hybrid polymer solar cells: in-situ-generated ZnO/poly(3-hexylthiophene) scaffolded by a TiO$_2$ nanorod array. J Phys Chem Lett 4:1983–1988
13. Lu H, Joy I, Gaspar RL, Bradforth SE, Bruchey L (2016) Iodide-passivated colloidal PbS nanocrystals leading to highly efficient polymer: nanocrystal hybrid solar cells. Chem Mater 28:1897–1906
14. Wang J, Zhang T, Wang D, Pan R, Wang Q, Xia H (2012) Influence of CdSe quantum dot interlayer on the performance of polymer/TiO$_2$ nanorod arrays hybrid solar cell. Chem Phys Lett 541:105–109
15. Xia H, Zhang T, Wang D, Wang J, Liang K (2013) Compositional interfacial modification in TiO$_2$ nanorod array/poly(3-hexylthiophene) hybrid photovoltaic devices. J Alloys Compd 575:218–222
16. Liu B, Aydi1 ES (2009) Growth of oriented single-crystalline rutile TiO$_2$ nanorods on transparent conducting substrates for dye-sensitized solar cells. J Am Chem Soc 131:3985
17. Wu F, Chen C, Zhao Y, Zhang H, Li X, Wu, Zhang T (2014) Changes of $V_{oc}$ in hybrid solar cells by TiO$_2$ nanocrystal with different crystallinity of shell. J Electrochem Soc 161:H593–H597
18. Wu F, Cui Q, Qiu Z, Liu C, Zhang H, Shen W, Wang M (2013) Improved open-circuit voltage in polymer/oxide-nanoray hybrid solar cells by formation of homogeneous metal oxide core/shell structures. ACS Appl Mater Interfaces 5:3246–3254
19. Ramsdale CM, Barker JA, Arias AC, MacKenzie JD, Friend RH, Greenham NC (2002) The origin of the open-circuit voltage in polymer/oxide-nanoray hybrid solar cells. J Appl Phys 92:4266–4270
20. Tan ZK, Johnson K, Vaynzof Y, Bakulin AA, Chua LL, Ho PKH, Friend RH (2013) Suppressing recombination in polymer photovoltaic devices via energy-level cascades. Adv Mater 25:4131–4138
21. Goh C, Scully SR, McGehee MD (2007) Effects of molecular interface modification in hybrid organic-inorganic photovoltaic cells. J Appl Phys 101:114503
22. Ruankham P, Macaraig L, Sagawa T, Nakazumi H, Yoshikawa S (2011) Surface modification of ZnO nanorods with small organic molecular dyes for polymer-inorganic hybrid solar cells. J Phys Chem C 115:23809–23816
23. Krüger J, Bach U, Grätzel M (2000) Modification of TiO₂ heterojunctions with benzoic acid derivatives in hybrid molecular solid-state devices. Adv Mater 12:447–451
24. Samadpour M, Irajizad A, Taghavinia N, Molaee M (2011) A new structure to increase the photostability of CdTe quantum dot sensitized solar cells. J Phys D Appl Phys 44:045103
25. Mihailetchi VD, Blom PiM, Hummelen JC, Rispens MT (2003) Cathode dependence of the open-circuit voltage of polymer: fullerene bulk heterojunction solar cells. J Appl Phys 94:6849
26. Kippelen B, Breddas JL (2009) Organic photovoltaics. Energy Environ Sci 2:251
27. Potscavage WJ, Yoo S, Kippelen B (2008) Origin of the open-circuit voltage in multilayer heterojunction organic solar cells. Appl Phys Lett 93:193308
28. Stevens DM, Speros JC, Hillmyer MA, Frisbie CD (2011) Relationship between diode saturation current and open circuit voltage in poly(3-alkylthiophene) solar cells as a function of device architecture, processing conditions, and alkyl side chain length. J Phys Chem C 115:20806
29. Lee YJ, Davis RJ, Lloyd MT, Provencio PP, Prasankumar RP, Hsu JWP (2010) Open-circuit voltage improvement in hybrid ZnO-polymer photovoltaic devices with oxide engineering. IEEE J Sel Top Quantum Electron 16:1587–1594
30. Siddiki MK, Venkatesan S, Galipeau D, Qiao Q (2013) Kelvin probe force microscopic imaging of the energy barrier and energetically favorable offset of interfaces in double-junction organic solar cells. ACS Appl Mater Interfaces 5:1279–1286
31. Ton-That C, Stockton G, Phillips MR, Nguyen TP, Huang CH, Cojocaru A (2008) Luminescence properties of poly-(phenylene vinylene) derivatives. Polym Int 57:496–501

Submit your manuscript to a SpringerOpen journal and benefit from:

- Convenient online submission
- Rigorous peer review
- Immediate publication on acceptance
- Open access: articles freely available online
- High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at ► springeropen.com