



Panchromatic response composed of hybrid visible-light absorbing polymers and near-IR absorbing dyes for nanocrystalline TiO₂-based solid-state solar cells

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ABSTRACT

In pursuit of panchromatic sensitizers for mesoporous TiO₂-based solid-state solar cells, a near-IR absorbing zinc phthalocyanine dye (coded TT1) was firstly adsorbed over relatively thin (~1 μm) TiO₂ mesoporous films and then a visible-light absorbing polymer [regioregular poly(3-hexylthiophene), P3HT] was incorporated into the mesopores as both a second sensitizer and a solid hole conductor. After optimizing some experimental parameters, these hybrid solid-state cells exhibited a clear panchromatic response, and an overall conversion efficiency of around 1% at full sun intensity.

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1. Introduction

Since an efficient dye-sensitized solar cell (DSSC) based on mesoporous TiO₂ films was reported by O'Regan and Grätzel [1], it has attracted significant attention throughout the world as an attractive alternative to conventional solar cells. Currently, the highest efficiency recorded by DSSCs has reached around 11% and the long-term stability has also improved greatly using hydrophobic dyes and robust electrolytes, thus almost entering into commercial markets [2]. Moreover, a variety of key materials (metal oxides, chromophores and hole transporters) and new concepts have been introduced continually, thus making this area more diverse and giving a momentum for further improvement [3,4]. One important issue raised recently in this area is to make an efficient *solid-state* cell showing a *panchromatic* response in photovoltaic conversions [4–6]. Due to intrinsic stability issues, the solid-type cells are considered to be more ideal than liquid counterparts for practical applications. However, the progress in finding an efficient solid-state hole conductor in DSSCs has been very slow and now only spiro-OMeTAD works well with general applicability for almost all the dyes, which were successfully tested in liquid-type DSSCs, while inorganic candidates such as CuSCN and CuI gave only

few good results [7,8]. Meanwhile, π-conjugated polymers have been applied successfully in many organic electronics including solar cells [9]. In particular, regioregular poly(3-hexylthiophene) (P3HT) could find a variety of applications in many areas due to its superior characteristics such as strong absorption in the visible range and high hole mobilities [10]. Recently, there have been some trials of using P3HT as both a sensitizer and a hole transportor under the structure of solid-state DSSCs; (1) without sensitizing dyes [11,12] and (2) with a visible-light absorbing dye (as a first sensitizer) between metal oxides and P3HT [13–15]. However, the overall power conversion efficiencies were relatively low and it was difficult to see clearly whether or not P3HT is doing its role as a second sensitizer due to a huge overlap of its absorption range with that of dyes used as a first sensitizer. If the energy ranges at which the two light-harvesting materials absorb strongly are different (for example, one for visible and the other for near-IR), it will be more straightforward to check their own functions and their combination looks ideal for making a cell showing a panchromatic response in light-to-current conversions. Recently, we have reported an efficient near-IR absorbing dye (coded TT1), which exhibited around 4% overall efficiencies with high IPCE value (about 80% at the maximum peak) on the basis of a liquid-type DSSC [6]. In this study, we have demonstrated all solid-state solar cells showing a clear panchromatic response by combining the efficient near-IR absorbing dye (TT1) on mesoporous TiO₂ films with the visible-light absorbing P3HT as both a second sensitizer and a hole conductor in the frame of solid-state DSSCs.

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2. Experimental

Photoelectrodes consisted of a TiO₂ film with a double layer structure. A compact blocking underlayer of spray-pyrolyzed titanium dioxide (ca. 150 nm thick) was deposited onto a cleaned conducting glass substrate (NSG, F-doped SnO₂, resistance 15 Ωsq⁻¹) to avoid a direct contact between FTO and P3HT. About 1 μm thick of TiO₂ mesoporous layers (from 20, 30, 60 nm-particulated TiO₂, Showa Titanium Company) were prepared by doctor-blading, and then the electrodes were treated with an aqueous solution of TiCl₄ using the typical procedures carried out in our laboratory for solid-state DSSCs [16,17]. Zinc phthalocyanine (TT1) dye was prepared according to our previous report [6], and its derivatization of nanocrystalline oxide films was obtained by immersing the TiO₂ electrode into the dye solution (0.05 mM in ethanol with 10 mM chenodeoxycholic acid, Cheno) for 4 h. TT1 dye-sensitized electrode was dipped for 30 min in diluted P3HT solution (regioregular P3HT from Rieke metals, dissolved in chlorobenzene at a concentration of 3 mg ml⁻¹), then dried in air and gently heated upto 50 °C to make some P3HT adsorbed onto TiO₂/TT1 dye, thus facilitating the later incorporation of P3HT more intimately into the mesopores [13]. Over the electrode of TiO₂/TT1/some P3HT, a 200 μl of high concentrated P3HT solution (16 mg ml⁻¹) was put and then incorporated into the mesopores by spin coating (two times), followed by annealing the film at 100 °C for 10 min under Ar flow. Finally, about 70 nm gold was evaporated onto the spin-casted polymers as a counter electrode (active area: 0.12–0.16 cm²). The measurements of photocurrent–voltage and incident photon-to-current conversion efficiency (IPCE) were done by following the same procedures as in our typical dye-sensitized systems. Transient absorption studies of TiO₂/TT1/P3HT were carried out as described previously [18]. More specifically, transient absorption data were collected using a highly sensitive microsecond absorption systems under N₂. Data was collected using an excitation wavelength of 670 nm, with pulse width 0.6 ns and pulse energy density of 60–80 μJ cm⁻² at 2 Hz repetition from a dye laser (Photon Technology International Inc. GL-301) pumped by a nitrogen laser (Photon Technology International Inc. GL-3300). Samples were probed at 980 nm using two monochromators and a quartz halogen lamp (Bentham, IL1) with a stabilized power supply (Bentham, 605). Probe light was detected by a silicon photodiode and the signal subsequently amplified and passed by electronic band-pass filters to improve signal to noise.

3. Results and discussion

Fig. 1 shows absorption spectra taken from P3HT polymers and TT1 dyes adsorbed over TiO₂ films (see the structures in the inset). The P3HT absorbs a broad range of visible light centered around 520 nm while the absorption peak of TT1 is around 680 nm with high molar extinction coefficient ($\epsilon = 160,000$) corresponding to the Q-band transition. Apparently, it looks ideal to combine P3HT and TT1 as a hybrid sensitizer for panchromatic response from visible to near-IR ranges.

Moreover, the energy levels of P3HT and TT1 are aligned favorably for charge transferring from the both to metal oxides (electron acceptor) or gold metals (hole-collecting electrode) (see Fig. 1 inset). In order to make regenerative solid-state cells, the flat or mesoporous TiO₂ films were prepared onto the FTO glass and then TT1 dyes were adsorbed via the carboxylate linker group onto the surface of TiO₂ as a first sensitizer, followed by incorporation of P3HT as both a second sensitizer and a hole conductor. In both cell structures (two-dimensional bilayer and three-dimensional mesoporous TiO₂/P3HT films), the dye inclusion between TiO₂ and P3HT was beneficial, especially, in increasing the short-circuit pho-

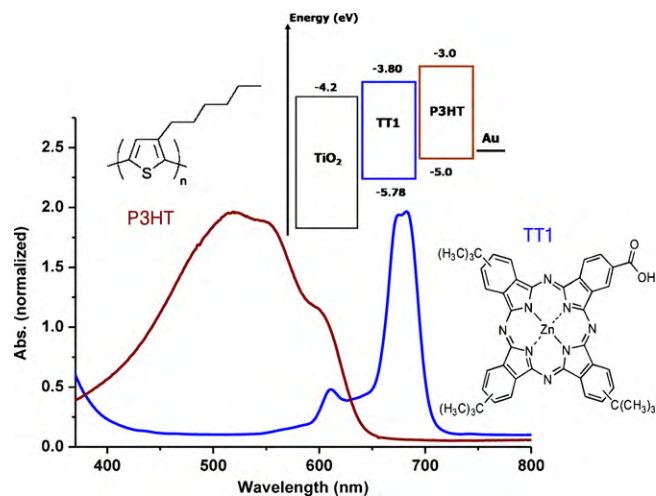


Fig. 1. Normalized absorption spectra of P3HT polymer (brown) and TT1 dye (blue) over TiO₂ films with their structures and energy band diagram in the inset. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

to currents, thus leading to superior overall efficiencies compared to TiO₂/P3HT cells without dyes (Table 1). The origin of those enhanced photocurrents is clearly seen in the IPCE data shown in Fig. 2; (1) when P3HT only is assembled inside the mesopores of TiO₂ film, some of P3HT placed near to the surface of TiO₂ are sensitizing a broad range of visible lights starting from its absorption onset, about 650 nm while the rest in the mesopores are transporting the as-generated holes in P3HT-sensitizers to the gold electrode. (2) By anchoring near-IR absorbing TT1 dyes between TiO₂ and P3HT, the photocurrents in the visible range were observed to increase about 70% compared to P3HT-only cells, with an extended response in the near-IR range coming from TT1 dye itself. The latter signal shown around 690 nm was confirmed to be from TT1 dyes by comparing that with only TT1 dye-sensitized solid-state cell using spiro-OMeTAD as a hole conductor (TiO₂/TT1/spiro-OMeTAD/Au) [17]. From two distinctive IPCE signals featured in the visible and near-IR range, respectively, it now looks straightforward that both P3HT polymer and TT1 dye are working effectively as sensitizers in different energy regions. The enhanced photocurrents of P3HT via the presence of TT1 dye can be ascribed to a few expected advantages of TT1/P3HT hybrid-sensitizer structures; (1) organic dyes anchored to the surface of TiO₂ could improve the wetting of the oxide surface by the hydrophobic polymer, thus leading to the increase of the interfacial contact area for charge separations. (2) TT1 dyes placed between TiO₂ and P3HT could act as an electronic mediator to increase the efficiencies of electron injection under the cascade band structures shown in the inset of Fig. 1. (3) TT1 dyes at the interface could make the TiO₂ surface and P3HT separated properly, thus preventing the direct contact and thereby

Table 1

A summarized data set of short-circuit currents, open circuit voltages, fill factors and overall conversion efficiencies from various cell structures based on FTO/flat or mesoporous TiO₂ films/(TT1 dye)/P3HT/Au.

TiO ₂	Dye	Polymer	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF	η (%)
Flat	No	P3HT	0.13	0.56	0.48	0.036
Flat	TT1	P3HT	0.22	0.55	0.58	0.099
Mesoporous (60 nm TiO ₂)	TT1	P3HT	2.18	0.64	0.53	0.73
Mesoporous (30 nm TiO ₂)	No	P3HT	1.26	0.64	0.46	0.37
Mesoporous (30 nm TiO ₂)	TT1	P3HT	2.86	0.74	0.48	1.01

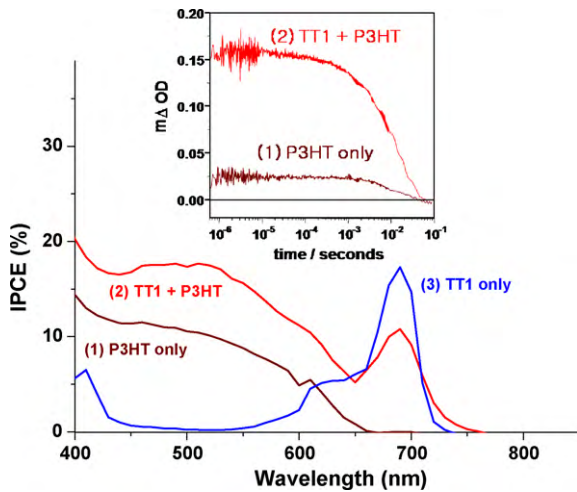


Fig. 2. IPCE spectra of three different sensitizers put between FTO/ $\sim 1 \mu\text{m}$ thick of 30 nm TiO_2 films and gold electrode: (1) P3HT polymer only (brown), (2) TT1 dye/P3HT polymer (red), and (3) TT1 dye/spiro-OMeTAD (blue). In the inset, transient absorption decays following the charge recombination reaction between photogenerated electrons in TiO_2 and holes of P3HT in $\text{TiO}_2/\text{P3HT}$ (1) and $\text{TiO}_2/\text{TT1}/\text{P3HT}$ (2). These data were obtained by pulsed laser excitation at 670 nm and monitoring the decay kinetics at 980 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

suppressing the charge recombination between them. (4) exciton energy transfer from P3HT to TT1 could be expected by a spectral overlap between the emission of P3HT and the absorption of TT1. Although the exact mechanism for enhanced photocurrents is not clear now, some of them or all appear to be contributing to the increase of P3HT-absorbed light-to-current conversion efficiencies. In addition to helping P3HT generate more currents, TT1 dye itself is converting near-IR incident lights to photocurrents as can be seen in IPCE signals around 690 nm where P3HT is not absorbing the incident light. These observations clearly show that both visible-light sensitizing P3HT polymer and near-IR-sensitizing TT1 dye are working effectively as a sensitizer with P3HT as a common hole conductor. When we checked the above-observed light-to-current conversion behavior with another typical visible-light sensitizing polymer (MEH-PPV) and near-IR-sensitizing squaraine dye (coded SQ1), the same results were seen with clear two distinctive peaks at each region (data not shown).

In this study, P3HT polymer is functioning both as a sensitizer and a hole transporting material. In particular, there have been few studies investigated so far about the hole-conducting role of P3HT under the structure of solid-state DSSCs. It has been demonstrated previously that one of the key parameters controlling the yield of dye regeneration at $\text{TiO}_2/\text{dye}/\text{organic}$ hole transporting material (HTM) heterojunctions is the driving force: $\Delta G_{\text{HTM-dye}} = \Delta G_{\text{HTM}} - \Delta G_{\text{dye}}$ [19]. As such, it is anticipated that the approximately 0.8 eV HOMO–HOMO energy offset as estimated using literature values for TT1 and P3HT [6,20] is sufficient to facilitate efficient hole transfer and subsequent dye regeneration. To investigate this, microsecond to millisecond transient absorption spectroscopy was employed to study the hole generation reaction at the $\text{TiO}_2/\text{TT1 dye}/\text{P3HT}$ heterojunction. The transient decay traces shown in the inset of Fig. 2 follow the charge recombination reaction between the photoinjected electrons in the TiO_2 and the polarons in the P3HT for the $\text{TiO}_2/\text{TT1 dye}/\text{P3HT}$ film (sample 2) and a $\text{TiO}_2/\text{P3HT}$ control sample (sample 1) used in this study. These data were obtained by monitoring the decay kinetics at 980 nm (polaron band of the P3HT) [21] following pulsed laser excitation of the TT1 dye at 670 nm. It is apparent that no rise in the decay kinetics of sample 2 are seen at short timescales indicating that the hole transfer reaction occurs on time scales faster than our instrument

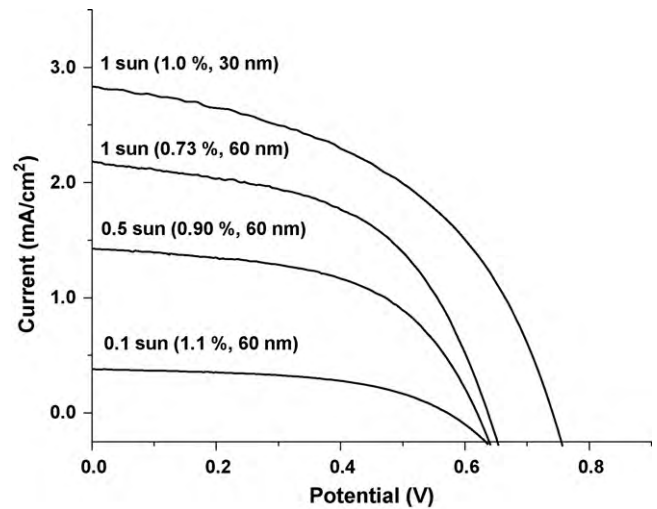


Fig. 3. Current–voltage curves measured from TT1/P3HT hybrid sensitizer placed between FTO/ $\sim 1 \mu\text{m}$ thick 60 or 30 nm TiO_2 films and gold under designated light intensities.

response (< 600 ns); this observation being consistent with previous studies [22]. Moreover, the amplitude of the signal at short time delays (magnitude of change in optical density $m\Delta\text{OD}$) in this figure is directly related to the concentration of P3HT polarons and thus the yield of hole transfer. It is apparent that sample 2 exhibits an approximately six times more generation of P3HT^+ when TT1 dye was present at the interface, clearly indicating that there is hole transfer from TT1 to P3HT following excitation of the TT1 dye.

In order to enhance light-harvesting capability by increasing the interfacial surface areas, three-dimensional mesoporous TiO_2 films with a thickness of about $1 \mu\text{m}$ were prepared and their photovoltaic performances were tested after incorporating TT1 dye and/or P3HT polymer (Table 1). When 20 nm-particulated TiO_2 films, which are typical ones in DSSCs, were tested firstly, it was difficult to get a reproducible data maybe due to a rather narrow pore size (less than 20 nm) for a complete infiltration of regioregular P3HT polymers. This kind of penetration problem of organic compounds into inorganic mesopores was also observed in typical solid-state DSSCs [17] and still remains as one urgent issue to be solved in that area. Moreover, regioregular P3HT has much bulkier structure than spiro-OMeTAD and looks more difficult to be incorporated down to the bottom electrode through three-dimensional irregular mesopores by spin-coating method [23]. Therefore, the relatively thin ($\sim 1 \mu\text{m}$) TiO_2 films with larger pore sizes were always observed to be better in photovoltaic performances than the typical 20 nm TiO_2 -based films; when 60 nm TiO_2 film (average pore size of 49 nm) was tested under different light intensities (Fig. 3), relatively good overall efficiencies ($\sim 1\%$) were observed over TT1/P3HT hybrid sensitizers. But, the short-circuited photocurrents were not proportionally increased vs. light intensities, which implies that the recombination process between the injected electrons into the conduction band of TiO_2 and holes in P3HT occurs more severely at higher light intensities. Although this 60 nm TiO_2 -composed film is taking advantage of a facile incorporation of P3HT polymers through a rather larger pores (~ 49 nm), the interfacial surface areas decreased to about one third compared to that of typical 20 nm TiO_2 film and the pore size also does not seem to be optimized if considering the exciton diffusion length (~ 10 nm) of P3HT. Therefore, the best overall efficiency at full sun intensity was obtained from 30 nm TiO_2 films (average pore size of 28 nm); a compromise between 20 and 60 nm TiO_2 films. This kind of pore size effect was also observed when spiro-OMeTAD was incorporated into PbS QD-sensitized mesopores [24]. Now, under standard

global AM 1.5 solar condition, the TT1/P3HT-sensitized cell over 1 μm thick of 30 nm TiO_2 film gave a short-circuit photocurrent density of 2.86 mA cm^{-2} , an open circuit voltage of 0.74 V, and a fill factor (ff) of 0.48, corresponding to an overall conversion efficiency η of 1.01%. Although we reached a relatively good overall efficiency of about 1% in this new-type of hybrid solar cell, there are still many parameters left for further optimizations. In particular, the infiltration of polymers into mesopores and its optimizations for improved exciton separations within mesopores appear to be critical in determining overall power conversion efficiencies and guaranteeing the reproducible results.

In this study, we have shown that a sort of panchromatic hybrid sensitizers made of near-IR absorbing TT1 dye and visible-sensitive P3HT polymer could generate photocurrents effectively at their own light-harvesting regions under the structure of solid-state DSSCs. This kind of combination from many promising dyes and polymers placed at different spatial positions in the working cell could open many interesting opportunities for testing charge- and/or energy transfer-based charge collections toward highly efficient all solid-state solar cells.

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