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Diketopyrrolopyrrole-Based Donor–Acceptor Copolymers as Organic Sensitizers for Dye Sensitized Solar Cells

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Received: September 29, 2009; Revised Manuscript Received: December 25, 2009

In this work diketopyrrolopyrrole based copolymers (PDPP-BBT and TDPP-BBT) containing a donor–acceptor structural unit have been explored as organic sensitizers for quasi-solid state dye sensitized solar cells. Polymer-sensitized solar cells (PSSC) fabricated utilizing PDPP-BBT and TDPP-BBT as the active layer resulted in a typical power conversion efficiency of 1.43% and 2.41%, respectively. The power conversion efficiency of PSSCs based on TDPP-BBT with use of TiCl₄-modified TiO₂ photoanode was about 3.06%, attributed to the reduced back recombination reaction and more charge carriers in the external circuit.

Introduction

In recent years, dye-sensitized solar cells (DSSCs) based on inorganic/organic hybrid materials gained significant attention as an alternative to conventional silicon-based solar cells.¹ These cells are very promising because of their low cost and high power conversion efficiency. The most widely used device architecture of conventional DSSCs typically contains the following key components: (i) a photoanode (mesoporous TiO₂ film), (ii) a sensitizer (dye), (iii) an electrolyte/hole transporter, and (iv) a counter electrode. The overall power conversion efficiency of DSSC is affected by many factors including the nanostructure organization of TiO₂.² The ordered assembly of TiO₂ provides percolating pathways for efficient electron transport to the electrode.³ In this context one-dimensional nanostructure was proven to be an effective way to increase the electron mobility by providing a large electron diffusion coefficient as compare to a TiO₂ nanoparticle thin film.⁴ The Ru(4,4'-dicarboxylic acid-2,2'-bipyridine)₂(NCS)₂ complex is frequently used as a sensitizer, which is anchored to the surface of semiconducting TiO₂ nanocrystals.⁵ In combination with mesoporous TiO₂ thin film and various dyes as a sensitizer, power conversion efficiencies up to 11% have been achieved.^{1,6,7} But still there is a lot of room to explore new materials to overcome the drawbacks of existing sensitizers. For example, Gratzel and co-workers^{8–13} have explored a large variety of ruthenium complexes for the application in DSSCs and observed that thiocyanate-containing ruthenium(II) complexes perform well in nanocrystalline TiO₂ DSSCs. These expensive and source limited ruthenium dyes can be replaced with environmentally friendly metal free organic sensitizers. As demonstrated by many research groups, the metal free organic sensitizers have many advantages such as lower cost, easier processing, and higher molar extinction coefficient.^{14–22} Most of the metal free organic sensitizers used for DSSCs show the character of both electron donor (D) and electron acceptor (A) linked with a π conjugation

bridge.^{23–31} Generally, organic sensitizers for excellent DSSCs are required to possess broadband intense spectral absorption in the visible light region and also have suited the lowest unoccupied molecular orbital (LUMO) energy level with the energy of the conduction band edge of nanocrystalline metal oxide semiconductor for efficient electron injection. Various groups have explored conjugated polymers as a sensitizer to meet all the above requirements.^{32–38} We directed our attention toward the synthesis of conjugated polymers containing donor–acceptor–donor structures and explore these materials as a sensitizer in solar cells. The energy levels (HOMO–LUMO) can be controlled by introducing alternating electron-rich and electron-deficient units in the polymer backbone. These materials were reported to have large absorption coefficients and tunable band gaps that cover the whole visible and near-IR spectrum.^{39,40} These properties are essential for DSSCs since the high efficiency can only be achieved when the excited state charge transfer from the polymer to the photoanode is allowed and the photo-oxidized polymer can be easily reduced by the electrolyte. Up to now, the efficiencies of DSSCs based on conjugated polymers remain low.^{41–43} In the present work, we have explored diketopyrrolopyrrole-based conjugated copolymers for the first time as a sensitizer in solar cells.

Although the COOH group is a prime requisite to anchor on the TiO₂ surface, other reactive functional group such as –OH or C=O are also capable of anchoring on the TiO₂ surface.^{44,45} The polymers used in this study exhibit C=O groups in their backbone, hence the polymers can adsorb on the TiO₂ surface, as a result electrons can be injected from the excited state of polymers into the conduction band of TiO₂ as observed in the case of a carboxylated polythiophene.⁴²

Fabrication of Polymer-Sensitized Solar Cells. TiO₂ paste was prepared by slowly adding 1 g of TiO₂ powder (P25, Degussa) to 0.2 mL of acetic acid, 1 mL of water, and 60 mL of ethanol, then this mixture was sonicated for 3 h. Finally Triton X-100 was added and the well-dispersed colloidal paste was coated over FTO glass by the doctor blade technique. The TiO₂-coated FTO electrodes were sintered at 450 °C for 30 min. The polymer was dissolved in chloroform solution and the TiO₂ electrode was immersed into the solution for 10 h and after the sensitization, the electrode was washed. Quasi-solid state

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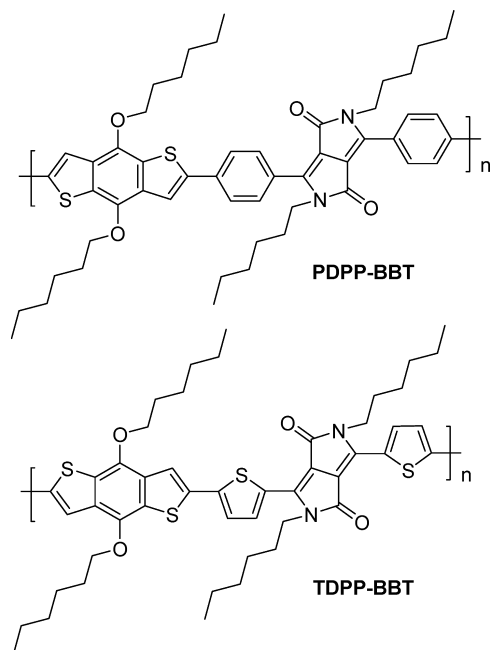


Figure 1. Chemical structure of PDPP-BBT and TDPP-BBT.

polymer electrolyte was prepared by adding 0.083 g of P25 TiO₂ powder, 0.1 g of LiI, 0.019 g of I₂, 0.264 g of PEO, and 44 μ L of 4-*tert*-butylpyridine to a (1:1) acetone/propylene carbonate solution. Finally the electrolyte was spin coated over the polymer-sensitized TiO₂ electrode.

To prepare the platinum counter electrode, H₂PtCl₆ solution in isopropanol (2 mg/mL) was deposited onto the FTO glass substrates and sintered at 400 °C for 30 min. The polymer-sensitized solar cells were fabricated by sandwiching the electrolyte between the polymer-sensitized photoanode and counter electrode.

The current–voltage (*J–V*) characteristics of these devices were measured in the dark and under illumination by a semiconductor parameter analyzer (Keithley 4200-SCS). A xenon light source (Oriel, USA) was used to give an irradiance of 100 mW/cm² (equivalent to AM1.5) at the surface of the device. The photoaction spectrum of the devices was measured with a monochromator (Spex 500 M, USA) and the resulting photocurrent was measured with a Keithley electrometer (model 6514), which is interfaced to the computer by LABVIEW software.

Results and Discussion

In the present study, we have used two diketopyrrolopyrrole (DPP)-based copolymers with different donor (phenyl and thiophene in DPP core) segments as organic sensitizers for the quasi-solid state DSSCs and the chemical structures are shown in Figure 1. The synthesis and characterization of these two copolymers, i.e., PDPP-BBT and TDPP-BBT, is reported elsewhere.⁴⁶

Figure 2 shows the UV–visible spectra of PDPP-BBT and TDPP-BBT thin films deposited from chloroform solution. The absorption spectra of these copolymers cover the entire solar spectrum. The PDPP-BBT and TDPP-BBT exhibit an intra-molecular charge transfer (ICT) band at 563 and 655 nm, respectively. Both the copolymers show broad absorption spectra with an extended absorption edge in the solid state. The optical band gaps of these polymers has been estimated from the absorption edge of the film, using $E_g^{op} = 1240/\lambda$, and are 1.70

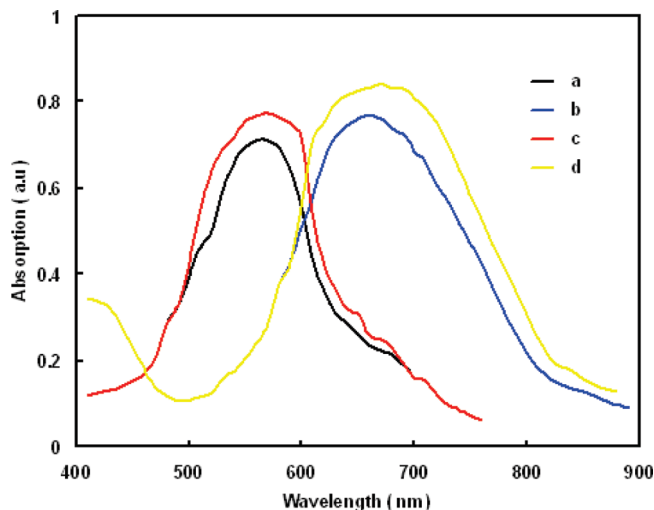


Figure 2. Absorption spectra of thin films of (a) PDPP-BBT and (b) TDPP-BBT, (c) PDPP-BBT, and (d) TDPP-BBT adsorbed on TiO₂ films.

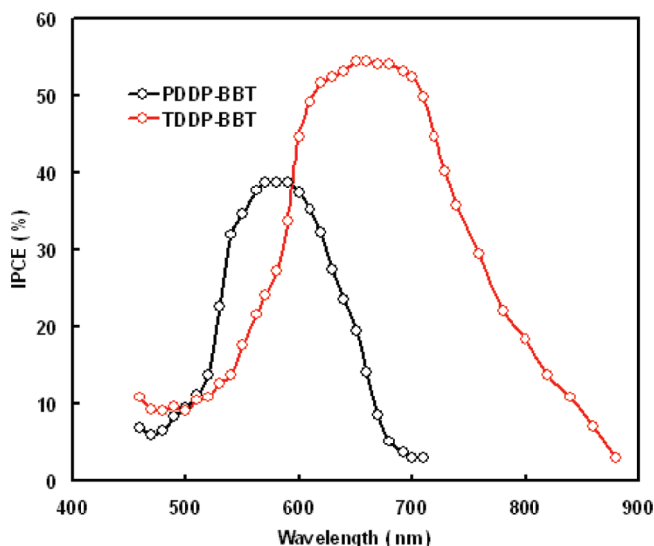


Figure 3. IPCE spectra of the quasi-solid state DSSCs based on PDPP-BBT and TDPP-BBT as sensitizers.

and 1.43 eV for PDPP-BBT and TDPP-BBT, respectively. Figure 2 also shows the normalized absorption spectra of copolymers adsorbed on TiO₂ film. In comparison to the absorption spectra of copolymer films, the absorption on the TiO₂ film was broadened and slightly red-shifted in both cases, indicating that both copolymers were assembled on the TiO₂ film in a monolayer state. The C=O groups at the backbone of the polymers are capable of anchoring on the surface of TiO₂.⁵³

Figure 3 shows the IPCE spectra obtained from DSSCs with use of PDPP-BBT and TDPP-BBT as sensitizers. The IPCE value (~54%) for the TDPP-BBT based cell is higher than that of the PDPP-BBT based cell. The IPCE spectra of the TDPP-BBT based device confirm the analysis for the absorption spectra of TDPP-BBT has a red-shifted and broadened light response as compared to that of PDPP-BBT. As the relatively narrowed absorption peak is one of the main drawbacks of organic dyes, this result indicates that the polymers could be potentially more effective sensitizers for DSSCs.

The current–voltage characteristics of the quasi-solid state polymer-sensitized solar cells under illumination intensity of 100 mW/cm² are shown in Figure 4. Both the devices were fabricated under identical conditions. The photovoltaic param-

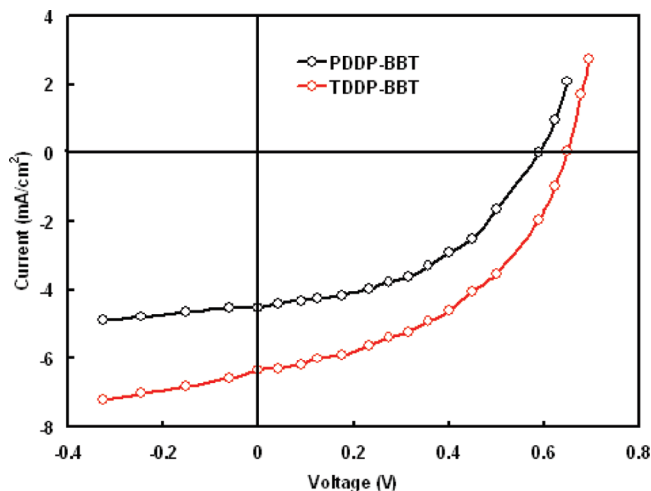


Figure 4. Current–voltage characteristics of the quasi-solid state DSSCs based on PDPP-BBT and TDPP-BBT sensitizers.

TABLE 1: Photovoltaic Parameters of the Quasi-Solid State Polymer-Sensitized Solar Cells

sensitizer	J_{sc} , ^a mA/cm ²	V_{oc} , ^b V	FF ^c	η , ^d %
PDPP-BBT	4.5	0.59	0.54	1.43
TDPP-BBT	6.3	0.66	0.58	2.41

^a Short circuit current. ^b Open circuit voltage. ^c Fill factor. ^d Power conversion efficiency.

eters estimated from these curves are summarized in Table 1. The power conversion efficiency of the solar cells with TDPP-BBT as sensitizer is higher than that of PDPP-BBT. It has been attributed to the improved light harvesting ability of TDPP-BBT as sensitizer due to excellent overlap with the solar spectrum and low band gap.

The IPCE at a wavelength is the production of three efficiencies,^{47,48} i.e., $IPCE(\lambda) = LHE(\lambda)\phi_{inj}\eta_c$, in which $LHE(\lambda)$ is the light harvesting efficiency at a wavelength λ , ϕ_{inj} is the electron injection efficiency, and η_c is the collection efficiency of the injected electrons at the photoanode. η_c is associated with (i) the electron transport within the TiO₂ network, (ii) the recombination of the injected electrons with the electrolyte (I_3^-), and (iii) the recombination of the injected electrons with the oxidized dye, and therefore should be independent of excitation wavelength. Since in both devices the photoanode, counter electrode, and polymer gel electrolyte are the same, the higher value of IPCE and power conversion efficiency are attributed to the improved light harvesting and the electron injection efficiency of the DSSCs based on TDPP-BBT rather than PDPP-BBT.

For both PDPP-BBT and TDPP-BBT, the LUMO energy level is energetically higher than the conduction band of TiO₂ (−4.2 eV), and consequently, electron injection from the single excited state of PDPP-BBT and TDPP-BBT into TiO₂ is energetically feasible. In addition, the oxidation potential of PDPP-BBT and TDPP-BBT is sufficiently more positive than the standard redox potential of iodine/iodide couple (0.34 V vs. Ag/AgCl), therefore, the photo-oxidized polymers could be efficiently reduced by the iodide ions. Moreover, the LUMO level of TDPP-BBT is higher than that of PDPP-BBT, resulting in more electron injection from TDPP-BBT into the conduction band of TiO₂ as compared to PDPP-BBT.

The open circuit voltage in the DSSCs can be expressed by following expression

$$V_{oc} = \left(\frac{kT}{q}\right) \ln \left[\frac{I_{inj}}{n_{cb}k_{et}[I_3^-]} \right]$$

where k is Boltzmann's constant, T is the absolute temperature, q is the electronic charge, I_{inj} is the injected electron flux from the sensitizers excited state into the conduction band of the TiO₂, n_{cb} is the density of the electron in the dark, k_{et} is the electron recombination rate in the back reaction, and $[I_3^-]$ is the concentration of iodide ions in the polymer gel electrolyte. Since more electrons are injected from the LUMO level of TDPP-BBT into the conduction band of the TiO₂, a higher open circuit voltage (V_{oc}) for the quasi-solid state DSSCs based on TDPP-BBT as compared to PDPP-BBT is observed.

Effect of Modified Anode on the Performance of DSSCs Based on TDPP-BBT. Post treatment with TiCl₄ was carried out according to the procedure reported in the literature.⁴⁹ A 0.05 M TiCl₄ aqueous solution was prepared in 2 M HCl solution. The sintered TiO₂ films were immersed into this solution and stored in an oven at 70 °C for 30 min. After being rinsed with distilled water and dried, the electrode was again sintered at 450 °C in an oven for 30 min. The resulting TiO₂ film was represented as TiCl₄ modified films.

The back electron transfer, i.e., electron leakage, which is the origin of the dark current, plays an important role in the photovoltaic performance of DSSCs.⁵⁰ The reduction of electron leakage is necessary to enhance the power conversion efficiency of DSSCs. The existence of uncovered TiO₂ sites in FTO, due to the porous nature of the TiO₂ film, mainly originates in the dark current. The porous structure provides pathways for commonly used redox electrolyte (i.e., I_3^- species) to penetrate through the porous film and contact the uncovered FTO surface. At these uncovered TiO₂ sites in FTO, the potential is thermodynamically favorable for the reduction of oxidative species, mainly I_3^- . This causes electron recombination and results in the loss of photocurrent. A comparison between the dark currents obtained from DSSCs with and without modified TiO₂ electrode can provide a qualitative measure for the current leakage due to the back electron transfer.^{50–52}

Figure 5 shows the onset potential of the dark current for the unmodified TiO₂ film at 0.38 V, while for the modified TiO₂ film, the onset potential shifted to 0.44 V. Furthermore, the dark current of the modified film increased much slower than that of the unmodified TiO₂ film. The increase in the onset potential and reduction in the dark current demonstrated that the modification of TiO₂ films reduces the uncovered surface area of the FTO surface forming a blocking layer and reduces the back electron transfer. Consequently, the suppression of electron leakage in the DSSCs with modified TiO₂ films led to an enhancement in the photovoltaic performance.

The performance of the quasi-solid state DSSCs with controlled film and modified films was characterized under the illumination intensity of 100 mW/cm². The photocurrent–voltage (J – V) characteristics for the DSSC with modified films are shown in Figure 6. The photovoltaic parameters, i.e., short circuit photocurrent (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (η) derived from the J – V characteristics are 7.16 mA/cm², 0.68 V, 0.63, and 3.06%, respectively.

The J_{sc} of the DSSC is mainly influenced by the dye loading amount and the electron transfer efficiency in the TiO₂ film.⁵⁰ We have estimated the amount of dye loading by desorbing the adsorbed dye from the photoelectrodes into a NaOH ethanolic solution and then measured the absorbance of the

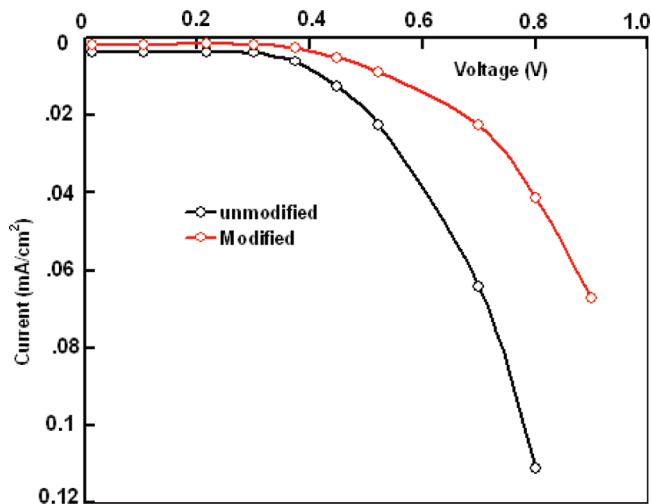


Figure 5. Dark current–voltage characteristics of quasi-solid state DSSCs based on TDPP-BBT as sensitizer with unmodified and modified TiO₂ electrode.

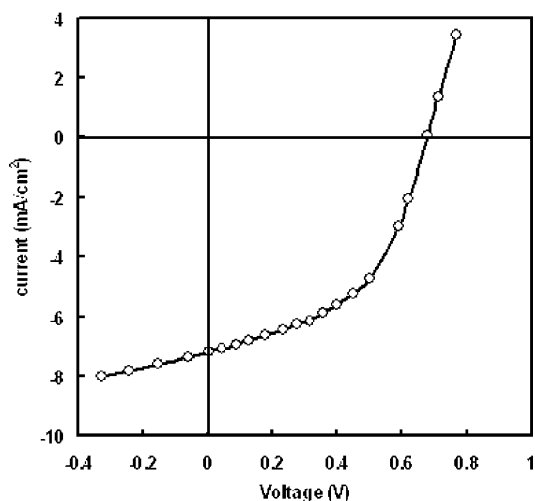


Figure 6. Current–voltage characteristics of quasi-solid state DSSCs based on TDPP-BBT as sensitizer with modified TiO₂ electrode under illumination.

solution. The calculated amounts of TDPP-BBT loading from the unmodified film and modified film were 5.25×10^{-7} and 5.30×10^{-7} mol/cm², respectively. This shows that the modification of the TiO₂ film does not significantly affect the adsorbed amount of TDPP-BBT. The similar dye loading amount implies that under the same illumination conditions, the concentration of photoinjected electron from the dye to the TiO₂ conduction band will be the same. Therefore, the main factor influencing the J_{sc} of the DSSC investigated should be the charge recombination at FTO/electrolyte interfaces. In DSSCs with modified TiO₂ film, the recombination sites (uncovered TiO₂ sites in FTO) are reduced and subsequently the charge recombination in the DSSCs is effectively suppressed as seen in the dark current measurements (Figure 5). Therefore, the increase in the J_{sc} for the modified film may be associated with the improved electron transfer efficiency in the TiO₂ film. As a result, more electrons are transferred to the external circuit.

Since the amount of the photogenerated electrons is directly proportional to the incident illumination intensity, the variation of short circuit photocurrent (J_{sc}) with the illumination intensity (P_{in}) can be used to obtain information about the amount of photogenerated electrons contributing to the photocurrent and also electron transfer kinetics. Figure 7 shows that J_{sc} of the

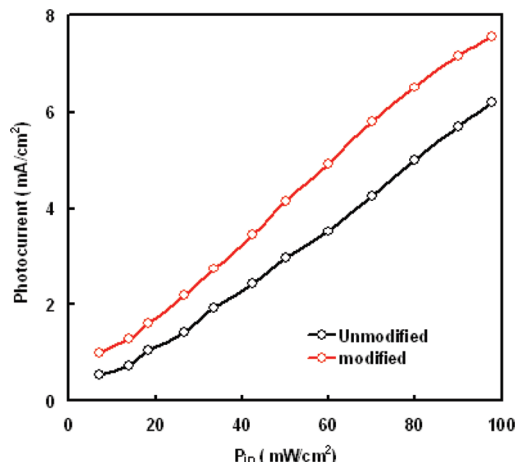


Figure 7. Variation of photocurrent with illumination intensity for quasi-solid state DSSCs based on TDPP-BBT as sensitizer with modified TiO₂ electrode under illumination.

DSSCs with porous TiO₂ and the modified TiO₂ were directly proportional to P_{in} . This indicates that the current density for both DSSC's was limited by the P_{in} , rather than the electron transfer processes, such as mass transport of I₃[−] or electron transfer at the counter electrode. The slope for the modified TiO₂ (i.e., 0.12) is 25% higher than that for the unmodified TiO₂ (0.096) electrode, which indicates that 33% more electrons are collected from the same amount of photogenerated electrons at the FTO surface. This confirms that the use of the modified TiO₂ electrode in DSSCs facilitates the electron transfer at the porous TiO₂/FTO interface, resulting in an increase in collection efficiency.

Conclusions

Diketopyrrolopyrrole-based copolymers PDPP-BBT and TDPP-BBT, containing a donor–acceptor structural unit, were synthesized and used as organic sensitizer to fabricate the quasi-solid state DSSCs. The DSSCs yield an overall power conversion efficiency about 1.43% and 2.41% for PDPP-BBT and TDBBT-BBT, respectively. Better power conversion efficiency of TDPP-BBT based DSSCs comes from the red-shifted and broadened absorption spectrum for the TDPP-BBT relative to PDPP-BBT and also more electron injection from the LUMO level of TDPP-BBT into the conduction band of TiO₂ as it lies more positive as compared to that of PDPP-BBT. The overall power conversion efficiency has been further increased when the TiCl₄-modified TiO₂ electrode photoanode is used to fabricate the DSSCs. This increase has been attributed to the reduction in the back recombination of injected electrons with I₃[−] in the electrolyte.

Acknowledgment. The authors acknowledge the Department of Science and Technology, New Delhi, India for financial support.

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