



A multifunctional ruthenium based dye for hybrid nanocrystalline titanium dioxide/poly(3-hexylthiophene) solar cells



Arumugam Pirashanthan^a, Thanishaichelvan Murugathas^a, Kadarkaraisamy Mariappan^b, Punniamoorthy Ravirajan^a, Dhayalan Velauthapillai^c, Shivatharsiny Yohi^{d,*}

^a Department of Physics, University of Jaffna, Jaffna 40000, Sri Lanka

^b Department of Chemistry, University of South Dakota, Vermillion, SD 57069, USA

^c Faculty of Engineering, Western Norway University of Applied Sciences, 5020 Bergen, Norway

^d Department of Chemistry, University of Jaffna, Jaffna 40000, Sri Lanka

ARTICLE INFO

Article history:

Received 24 April 2020

Received in revised form 13 May 2020

Accepted 14 May 2020

Available online 18 May 2020

Keywords:

Solar cell

Titanium dioxide

Poly(3-hexylthiophene)

Co-sensitizers

ABSTRACT

This work reports the influence of a Ru based dye (RuC) on enhancing the performance of nanocrystalline titanium dioxide (TiO₂)/Poly(3-hexylthiophene) (P3HT) solar cells. UV-Vis absorption spectra of TiO₂/P3HT and TiO₂/RuC/P3HT films reveal that the absorption spectrum of TiO₂/P3HT is broadened in the UV region due to the addition of the RuC dye. With pumping laser at the wavelength corresponds to maximum absorption of P3HT, photoluminescence (PL) of TiO₂/RuC/P3HT nanocomposite film was significantly quenched in comparison with PL of TiO₂/P3HT film which confirms the efficient exciton dissociation in TiO₂/RuC/P3HT. The insertion of the dye suppresses the dark current by two orders of magnitude in the cells while extends external quantum efficiency (EQE) spectra and hence increases the average short circuit current density (J_{sc}) from 2.52 (±0.25) to 6.44 (±0.43) mA/cm², resulting in three fold power conversion efficiency (PCE) increment from 0.73 (±0.06) to 2.35 (±0.13) %, under 100 mW cm⁻¹ (1 sun) illumination with AM 1.5 filter.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

Hybrid metal oxide/polymer solar cells have generated significant interest owing to their light weight, low cost, mechanical flexibility, and simple solution processing methods. Nanoporous TiO₂ and the relatively stable P3HT are one of most extensively studied materials combination in the field of hybrid solar cells [1,2]. However, it is well documented that the poor charge transport, limited spectral response of polymer, and poor compatibility between TiO₂ and polymer limits their PCE of TiO₂/polymer solar cells. Moreover, poor quality of the hybrid TiO₂-polymer interface significantly reduces the PCE of hybrid solar cells [3]. Engineering the polymer- TiO₂ interface is a well-known technique to improve the charge separation, collection, and transport in hybrid solar cells [4–7]. Range of novel organic/inorganic materials were employed as the interface modifiers which results with improved PCE of the hybrid solar cells. The interface modifiers studied in hybrid solar cells can be divided into three: (i) Self-Assembled Monolayers

(SAMs), (ii) large band gap metal oxides and (iii) light absorbing materials. SAMs, such as benzoic acid based molecules [4], and 3,4,5-methoxyphenylboronic acid, were shown to improve the PCE of the solar cells, mainly due to increased J_{sc} which is due to increased charge transfer yield by shifting the position of the conduction band of the porous TiO₂ relative to the polymer highest occupied molecular orbital (HOMO) level [4]. Further, SAMs increase open circuit voltage (V_{oc}) by acting as an insulating barrier to block the back electrons from TiO₂ to polymer. It was also reported that a large band gap alumina insulating monolayer at the TiO₂/P3HT interface slowdown the recombination kinetics and increase the charge transfer yield due to suppression of interfacial recombination [8]. However, these passive materials do not contribute to photocurrent generation, which is a main drawback, when a narrow absorption polymer like P3HT is used. Light harvesting materials such as organic dyes [1,2,9] and inorganic materials (CdS [5], and CdSe [10]) have been employed in hybrid TiO₂/polymer solar cells.

In this work, a multifunctional Ruthenium based dye was employed as an interface modifier. The corresponding device performance shows that insertion of dye improves the PCE by a factor of three, which is mainly due to the enhanced J_{sc}.

* Corresponding author.

E-mail addresses: dhayalan.Velauthapillai@hvl.no (D. Velauthapillai), srtharsha12@gmail.com, yshiva@univ.jfn.ac.lk (S. Yohi).

2. Materials and methods

The RuC dye was synthesised as reported elsewhere [11]. Refer [Supplementary information](#) for the details on solar cell fabrication and characterisation.

3. Results and discussion

The J-V characteristics of the completed solar cells fabricated with and without RuC dye under light and dark is shown in [Fig. 1](#). Ten working devices for each set were tested, and the average J_{SC} , V_{OC} , fill-factor, and PCE were analysed. The average PCE of the solar cells under illumination were found to increase from 0.73 (± 0.06) to 2.35 (± 0.13) % after dye modification, mainly due to the increased J_{SC} from 2.52 (± 0.25) to 6.44 (± 0.43) mA/cm^{-2} and V_{OC} from 0.53 (± 0.02) to 0.65 (± 0.02) V (Refer [Fig. S1](#) for the distribution of device merit parameters of 10 devices with and without RuC dye). No significant changes observed in the fill factor. The dark J-V curve clearly shows that the reverse saturation current of the dye modified device is an order of magnitude lower than that of $\text{TiO}_2/\text{P3HT}$ devices ([Fig. 1\(b\)](#)). It also clearly indicates that the ideality factor of the $\text{TiO}_2/\text{RuC}/\text{P3HT}$ heterojunction is much lower than that of $\text{TiO}_2/\text{P3HT}$. Low dark current and ideality factor

found in device with RuC interface modifier is a signature of suppression of interfacial recombination [12]. Reduced recombination could be one of the reasons behind the improved V_{OC} of the $\text{TiO}_2/\text{RuC}/\text{P3HT}$ solar cells under illumination [4,8,12].

[Fig. 2](#) shows the absorption spectra of the $\text{TiO}_2/\text{P3HT}$ nanocomposite with and without RuC dye. The RuC dye has strong absorption in the visible and near U-V region while P3HT has a strong absorption in the visible region with an absorption peak at about 525 nm. The absorption of the $\text{TiO}_2/\text{RuC}/\text{P3HT}$ is extended towards the UV region due to incorporation of the dye. [Fig. 2\(b\)](#) clearly shows the insertion of RuC dye improves the spectral response. The significant increase in EQE values at the wavelength correspond to maximum absorption of RuC confirms the contribution of dye in current generation. It can also be noted that the EQE values beyond 530 nm are also increased with the addition of RuC dye. Therefore, it can be concluded that the insertion of dye significantly increases the photon to electron conversion of the P3HT polymer.

The carrier dynamics of the solar cells with or without dye was studied using PV transient measurements. The solar cells were excited using a 530 nm laser, and the voltage transient was recorded. [Fig. 3 \(a\)](#) shows the dye treatment increased the half lifetime of the carriers to 25 ms which is four times less than that of

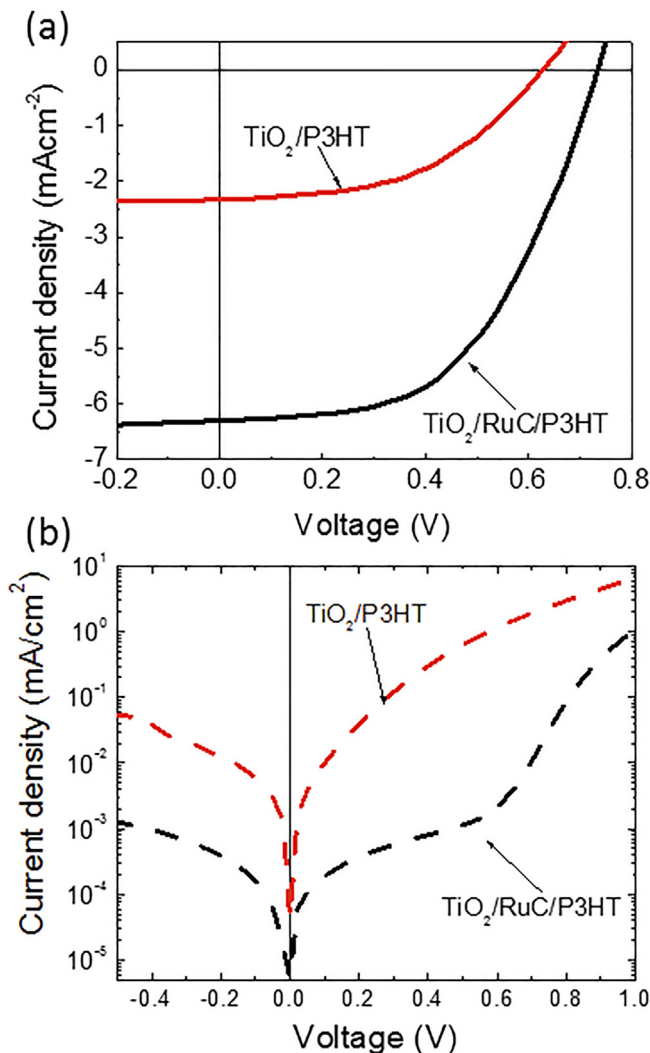


Fig. 1. J-V characteristics of $\text{TiO}_2/\text{P3HT}$ solar cells with and without RuC dye (a) under illumination (1 sun) with AM1.5 filter and (b) in dark.

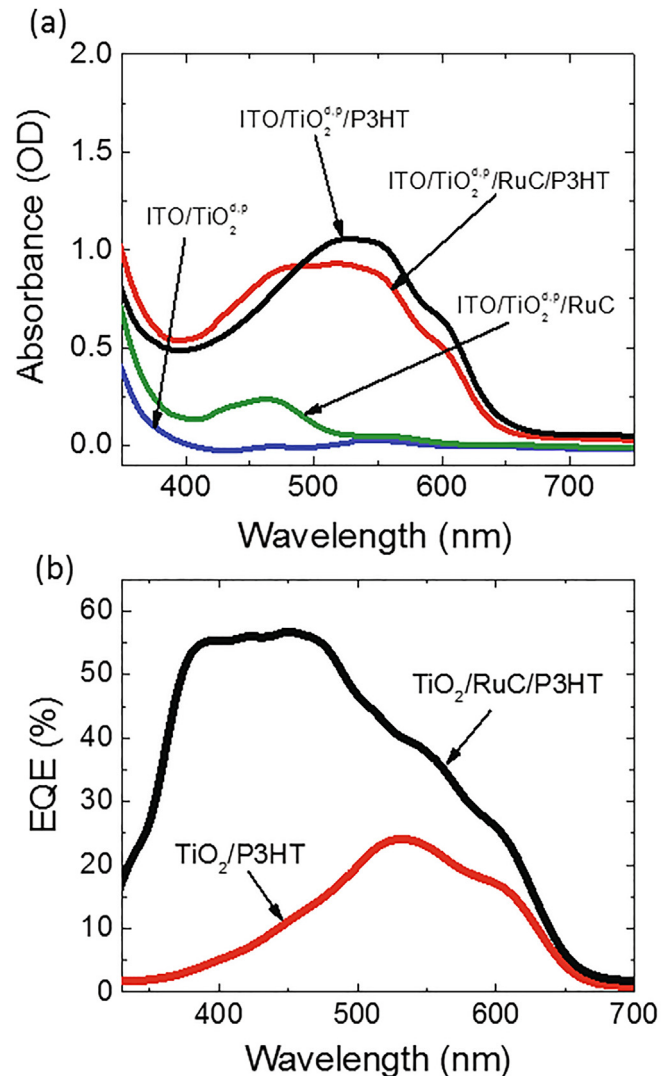


Fig. 2. (a) Absorption spectra of ITO/TiO_2 , $\text{ITO}/\text{TiO}_2/\text{RuC}$, $\text{ITO}/\text{TiO}_2/\text{P3HT}$ and $\text{ITO}/\text{TiO}_2/\text{RuC}/\text{P3HT}$ layer and (b) EQE spectra of $\text{TiO}_2/\text{P3HT}$ and TiO_2/RuC solar cells.

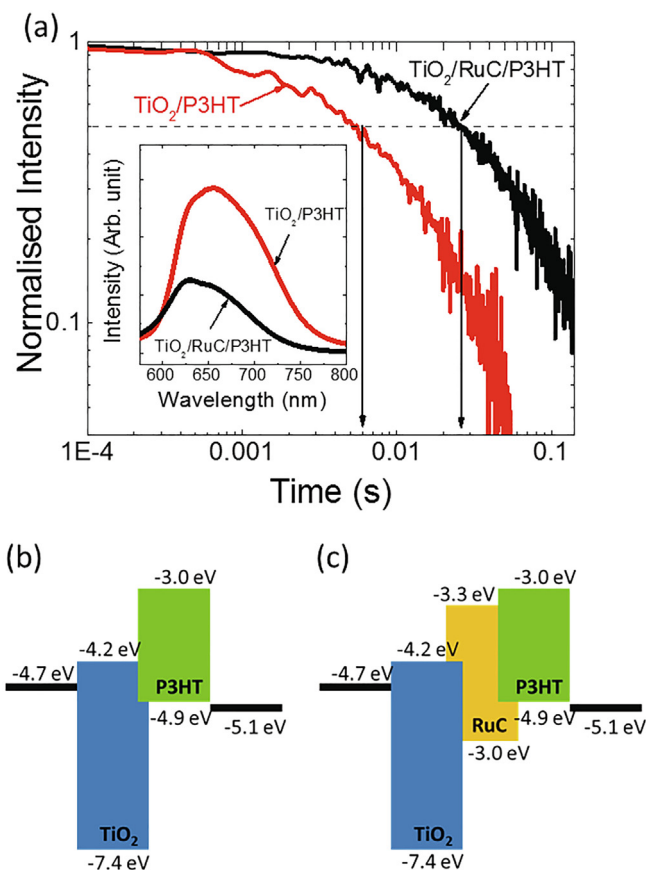


Fig. 3. (a) Normalised double logarithmic photovoltaic decay of TiO₂/P3HT and TiO₂/RuC/P3HT cells (inset: PL spectra of TiO₂/P3HT, TiO₂/RuC/P3HT films) and proposed Energy band diagram of (b) TiO₂/P3HT and (c) TiO₂/RuC/P3HT solar cells.

the structure without dye. This indicates that the charges excited in P3HT layer lives longer with the addition of dye at the interface. Hence, it can be concluded that the mobility and diffusion length of the P3HT film is enhanced with dye modification [13]. This could be the potential reason behind the improved EQE at the wavelengths beyond 530 nm, which is from the excitons of P3HT. PL spectra of the films were also recorded by exciting the film by a 530 nm laser to selectively excite the polymer and not the dye. The inset of Fig. 3 (a) shows that the PL spectra of TiO₂/P3HT film with or without dye resembles emission spectra of P3HT. However, a trace of luminescent signal found at maxima of 630 nm with the TiO₂/RuC/P3HT indicates the signature of RuC dye. In addition, the photoluminescent of TiO₂/P3HT nanocomposite film is quenched by a factor of two after dye addition. The quenching of P3HT emission denotes the enhanced exciton dissociation at the interface of TiO₂ nanocrystals and P3HT [14].

Based on the experimental results, and our previous works [4,15] on TiO₂/P3HT solar cells, the band diagram of the TiO₂/P3HT and TiO₂/RuC/P3HT solar cells were proposed as shown in Fig. 3(b). Since HOMO level of P3HT, and the CB of TiO₂ are close to each other, there should be a physical barrier to block back electron transfer from CB to HOMO [4]. The position of HOMO and lowest unoccupied molecular orbital level of the RuC dye on TiO₂/P3HT interface is expected to reduce the back-electron transfer which is reflected in the reduced dark current and improved V_{OC} found in TiO₂/RuC/P3HT devices. Overall, the insertion of the RuC dye at the TiO₂-P3HT interface improves the PCE by a factor of three by improving the spectral response, reducing the back-electron transfer and by improving the carrier lifetime in the TiO₂/P3HT nanocomposite solar cells.

4. Conclusion

This study showed that Ruthenium based RuC dye plays multiple roles in the TiO₂/P3HT solar cells, via extending the spectral response by contributing carrier generation in near UV region, and blocking back electron transfer as evidenced by absorption, photoluminescence, dark J-V and PV transient measurements. Optimised cell with RuC dye showed an average PCE of 2.35 (± 0.13)% under light which is a factor of three higher than the corresponding control.

Funding

This research was funded by CBERC and HRNCT projects (<http://project.jfn.ac.lk/hrnct/>).

CRediT authorship contribution statement

Arumugam Pirashanthan: Methodology, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization. **Thanihachelvan Murugathas:** Conceptualization, Methodology, Formal analysis, Data curation, Writing - original draft, Visualization. **Kadarkaraisamy Mariappan:** Conceptualization, Methodology, Validation, Resources, Writing - review & editing. **Punniamoorthy Ravirajan:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Dhayan Velauthapillai:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Shivatharsiny Yohi:** Conceptualization, Methodology, Validation, Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2020.127997>.

References

- [1] W.P. Liao, S.C. Hsu, W.H. Lin, J.J. Wu, Hierarchical TiO₂ nanostructured array/P3HT hybrid solar cells with interfacial modification, *J. Phys. Chem. C* 116 (2012) 15938–15945, <https://doi.org/10.1021/jp304915x>.
- [2] M. Planells, A. Abate, H.J. Snaith, N. Robertson, Oligothiophene interlayer effect on photocurrent generation for hybrid TiO₂/P3HT Solar Cells, *ACS Appl. Mater. Interfaces* 6 (2014) 17226–17235, <https://doi.org/10.1021/am505053z>.
- [3] D. Wang, H. Tao, X. Zhao, T. Zhang, J. Han, TiO₂/P3HT hybrid solar cell with efficient interface modification by organic and inorganic materials: a comparative study, *J. Nanosci. Nanotechnol.* 16 (2016) 797–801, <https://doi.org/10.1166/jnn.2016.10799>.
- [4] S. Loheeswaran, M. Thanihachelvan, P. Ravirajan, J. Nelson, Controlling recombination kinetics of hybrid poly-3-hexylthiophene (P3HT)/titanium dioxide solar cells by self-assembled monolayers, *J. Mater. Sci. Mater. Electron.* 28 (2017) 4732–4737, <https://doi.org/10.1007/s10854-016-6116-7>.
- [5] M. Thanihachelvan, M.M.P. Sri Kodikara, P. Ravirajan, D. Velauthapillai, Enhanced performance of nanoporous titanium dioxide solar cells using cadmium sulfide and poly(3-hexylthiophene) co-sensitizers, *Polymers (Basel)* 9 (2017) 467, <https://doi.org/10.3390/polym9100467>.
- [6] C. Goh, S.R. Scully, M.D. McGehee, Effects of molecular interface modification in hybrid organic-inorganic photovoltaic cells, *J. Appl. Phys.* 101 (2007), <https://doi.org/10.1063/1.2737977> 114503.
- [7] K. Balashangar, S. Paranthaman, M. Thanihachelvan, P.A. Amalraj, D. Velauthapillai, P. Ravirajan, Multi-walled carbon nanotube incorporated nanoporous titanium dioxide electrodes for hybrid polymer solar cells, *Mater. Lett.* 219 (2018) 265–268, <https://doi.org/10.1016/j.matlet.2018.02.088>.

- [8] S. Loheeswaran, K. Balashangar, J. Jevirshan, P. Ravirajan, Controlling recombination kinetics of hybrid nanocrystalline titanium dioxide/polymer solar cells by inserting an alumina layer at the interface, *J. Nanoelectron. Optoelectron.* 8 (2013) 484–488, <https://doi.org/10.1166/jno.2013.1514>.
- [9] J. Weickert, F. Auras, T. Bein, L. Schmidt-Mende, Characterization of interfacial modifiers for hybrid solar cells, *J. Phys. Chem. C* 115 (2011) 15081–15088, <https://doi.org/10.1021/jp203600z>.
- [10] J. Wang, T. Zhang, D. Wang, R. Pan, Q. Wang, H. Xia, Influence of CdSe quantum dot interlayer on the performance of polymer/TiO₂ nanorod arrays hybrid solar cell, *Chem. Phys. Lett.* 541 (2012) 105–109, <https://doi.org/10.1016/j.cplett.2012.05.074>.
- [11] S. Rasalingam, R. Peng, C.M. Wu, K. Mariappan, R.T. Koodali, Robust and effective Ru-bipyridyl dye sensitized Ti-MCM-48 cubic mesoporous materials for photocatalytic hydrogen evolution under visible light illumination, *Catal. Commun.* 65 (2015) 14–19, <https://doi.org/10.1016/j.catcom.2015.02.019>.
- [12] G.J.A.H. Wetzelaer, M. Kuik, P.W.M. Blom, Identifying the nature of charge recombination in organic solar cells from charge-transfer state electroluminescence, *Adv. Energy Mater.* 2 (2012) 1232–1237, <https://doi.org/10.1002/aenm.201200009>.
- [13] K. Prashanthan, T. Thivakarasarma, P. Ravirajan, M. Planells, N. Robertson, J. Nelson, Enhancement of hole mobility in hybrid titanium dioxide/poly(3-hexylthiophene) nanocomposites by employing an oligothiophene dye as an interface modifier, *J. Mater. Chem. C* 5 (2017) 11758–11762, <https://doi.org/10.1039/c7tc02225e>.
- [14] K. Kumari, U. Kumar, S.N. Sharma, S. Chand, R. Kakkar, V.D. Vankar, V. Kumar, Effect of surface passivating ligand on structural and optoelectronic properties of polymer : CCdSe quantum dot composites, *J. Phys. D. Appl. Phys.* 41 (2008), <https://doi.org/10.1088/0022-3727/41/23/235409>.
- [15] A. Pirashanthan, T. Murugathas, N. Robertson, P. Ravirajan, D. Velauthapillai, A Quarterthiophene-based dye as an efficient interface modifier for hybrid titanium dioxide/poly(3-hexylthiophene)(P3HT) solar cells, *Polymers (Basel)* 11 (2019) 1752, <https://doi.org/10.3390/polym11111752>.