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Enhancement of hole mobility in Hybrid Titanium Dioxide / Poly(3-hexylthiophene) Nanocomposites by Employing an Oligothiophene dye as Interface Modifier

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This study focuses on influence of interface modifiers on charge transport of Hybrid Nanoporous Titanium dioxide (TiO₂) / Poly (3-hexylthiophene) (P3HT) nanocomposites by using time of flight technique. We found that the hole-mobility in the nanocomposites is about three orders of magnitude less than that of pristine P3HT. This may be due to poor infiltration of the polymer into the highly structured porous TiO₂ which in turn obstructs the charge transport of the carriers. However, hole-mobility in the nanocomposites is increased by an order of magnitude when ruthenium based dye either Z907 or N719 is introduced at the TiO₂ / P3HT interface. Surprisingly, electron-mobility of the composite is decreased upon dye treatment. We further observed that hole-mobility of nanocrystalline TiO₂ / P3HT composites treated with a 3-hexylthiophene derivative with a cyanoacrylic acid group [(E)-2-Cyano-3-(3',3'',3'''-triethyl-[2,2':5',2'':5'',2''':5''']-quaterthiophene)-5-yl)acrylic acid] (4T) is increased over $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is over two orders of magnitude higher than the hole-mobility found in untreated nanocomposites. This trend in hole-mobility is consistent with corresponding current density (J) – voltage (V) characteristics under illumination of TiO₂ / P3HT devices with or without dye interface layer. The higher hole-mobility found in 4T dye treated TiO₂ / P3HT nanocomposite is assigned to passivation of surface traps by the dye as well as improved packing of the polymer with the nanocrystals through effective inter-chain interactions of 4T with P3HT.

Introduction

Organic photovoltaic devices based on metal oxide/polymer nanocomposites have attracted extensive interest due to their high mechanical stability and the multiple routes available to control the interface morphology.¹⁻⁵ However performance improvements are needed to improve the power conversion efficiency of photovoltaic devices, which have until now been limited by poor infiltration of conjugated polymers into porous metal oxide films⁶ and by poor charge transport in metal oxide/ polymer nanocomposites.^{7,8} Studies of transport properties are of fundamental importance in interpreting the basic physics in molecular PV devices⁹, in particular, the collection efficiency of photogenerated charges, and thus in enhancing the performance of such devices. It is generally difficult to determine charge carrier mobility uniquely^{10,11,12} in organic or hybrid semiconductors because of the high degree

of energetic (diagonal) and structural (off-diagonal) disorder. Time of flight (TOF) transient photocurrent is an established technique^{13,14,15} for mobility measurement in high-resistivity materials that allows these types of disorder to be quantified. Although a few independent studies have reported electron mobility in porous TiO₂⁷ and hole-mobility in poly(3-hexylthiophene) (P3HT)^{12,16}, no TOF studies of TiO₂ / P3HT nanocomposites have been reported so far. Transport in organic/inorganic nanocomposites is interesting because the combination of materials may affect charge transport in different ways, for example, through the restriction of charge percolation pathways, the effect of composite on molecular packing in the organic component, and the effect of interactions between charge carriers and the interface.

Several strategies have been used to modify the metal oxide surface in order to improve electronic properties of metal oxide/polymer hybrid materials, including the use of CdS quantum dots (QDs)¹⁷ and control of polymer alignment within pores of the oxide structure.¹⁸ It has also been reported that a thin overlayer of alumina¹⁹ retards recombination kinetics in hybrid TiO₂-P3HT solar cells as well as in dye sensitized solar cells^{20,21,22} and thus improves the overall cell performance. More recently, it has been shown that overall device performance of TiO₂ / polymer solar cells can be enhanced by more than a factor of two using a self-assembled monolayer²³ on TiO₂ nanoparticles with permanent dipole pointing towards the TiO₂ surface or pointing towards polymer when compared

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to a control device with no interface modifiers. It has also been demonstrated that inter dye hole-transport^{24,25,26} may contribute to current collection in solid-state dye-sensitized solar cells.

In the present work, we focus on studying the effect on hole transport in hybrid titanium dioxide / polythiophene (P3HT) nanocomposites of sensitizing the surface of the titanium dioxide with a monolayer of conjugated dye molecule, using ruthenium (Ru) based dyes (Z907 and N719) and a carboxylated thiophene oligomer, (E)-2-Cyano-3-(3',3'',3'''-triethyl-[2,2':5',2'':5'',2'''-quaterthiophene]-5-yl) acrylicacid (4T)²⁷ as interface modifiers. The chemical structures and full names of the dyes used in this study are shown in Figure 1. We use TOF as a tool to determine the carrier mobilities of the nanocomposites with or without interface modifiers. We find that the addition of the modifier increases the TOF hole mobility by up to two orders of magnitude. The effect of interface properties on the electronic properties of an adjacent semiconductor is more broadly relevant, for example, to the phenomena of charge recombination or charge trapping at interfaces in electronic devices. The finding is therefore relevant to the understanding and control of interfaces in organic and hybrid electronic devices.

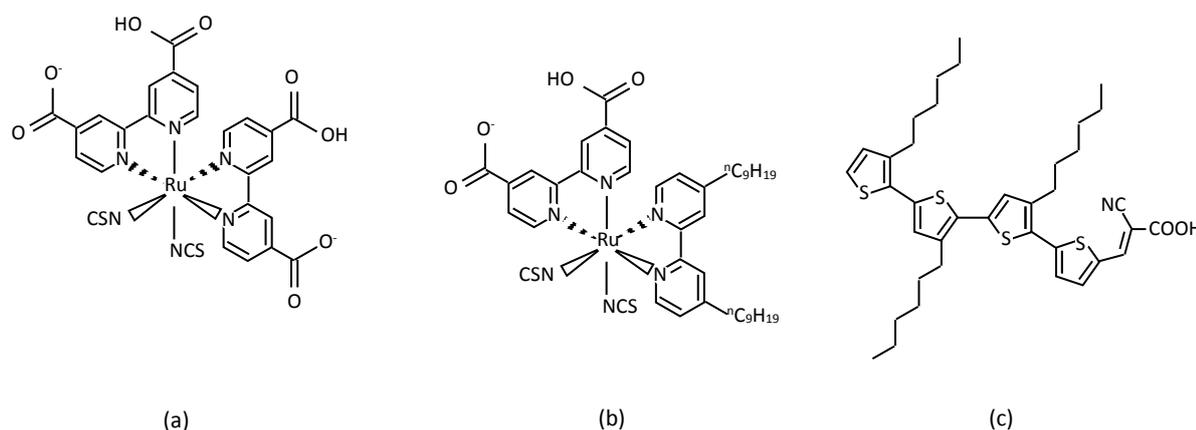


Figure 1. Chemical structure of (a) Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) (N719), (b) Terabutylammonium cis-Bis(isothiocyanato)(2,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2'-bipyridyl)ruthenium(II) (Z907) and (c) (E)-2-Cyano-3-(3',3'',3'''-triethyl-[2,2':5',2'':5'',2'''-quaterthiophene]-5-yl)acrylicacid(4T).

Experimental

Sample Preparation

The Samples were prepared on patterned Indium Tin Oxide (ITO) coated glass substrates (12 mm × 12 mm, 10 Ω/square), which were cleaned similarly to those reported elsewhere.²⁸ The substrates were then covered with a dense TiO₂ hole-blocking layer of 50 nm thickness by spray pyrolysis. For deposition of porous TiO₂ layer, TiO₂ paste (DSL 18NRT, Dyesol) having colloids of ~20 nm diameter was dissolved in tetrahydrofuran (THF) (180 mg/ml) and deposited on ITO substrates already coated with a dense TiO₂ layer by spin coating TiO₂ / THF solution (180 mg/ml) followed by sintering at 450 °C. The dye was then introduced at the polymer / TiO₂

interface by first heating the porous TiO₂ films at 110 °C for 10 minutes to remove surface water, followed by dipping the porous TiO₂ films in respective 0.3 mM solution of dye (Z907; Mw=870.10, N719; Mw=1188.75 both purchased from Dyesol, or 4T, synthesized as described in ref.(27)) in a solvent consisting of acetonitrile : tert-butanol (1:1 by volume), for 14 hours. Samples were then rinsed in acetonitrile : tert-butanol solution and dried in nitrogen followed by dipping in P3HT polymer (Mn = 24,000; Mw=55,000; RR = 95% purchased from Merck Chemicals Ltd.) solution dissolved in chlorobenzene (2mg/ml), overnight at 120 °C prior to P3HT spin coating, in order to obtain an active layer thickness of about 1 μm. Subsequently, these samples were coated with an 40 nm layer of highly-conductive Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)(PEDOT:PSS)²⁹ by spin coating before depositing a Au top contact of 40 nm by thermal evaporation through a shadow mask under high vacuum. Finally, silver paste was applied and annealed to improve the contacts during measurements.

Characterization of the samples

The optical absorption spectra of Z907, N719 and 4T coated nanoporous TiO₂ electrodes and spectra of Z907, N719 and 4T treated TiO₂ samples that had been coated with P3HT by dip and spin coating were measured using a JENWAY-6800 UV-Vis spectrometer. For charge transport studies of the nanocomposite devices, completed as described above, charge pairs were generated optically with a frequency-doubled Nd:YAG laser (excitation wavelength 532 nm, pulse width less than 6 ns, energy per pulse ~ 10 μJ, repetition rate 1 Hz and nominal beam diameter 2-8 mm), illuminating through the ITO. The photocurrent transients were monitored with a TDS 1012B (Two channel Digital Storage oscilloscope) maintaining

the ITO terminal at positive potential for finding hole-mobility and at negative potential for electron mobility.

Results and discussion

Figure 2 (a) shows the optical absorption spectra of porous TiO₂ (600 nm) / dye (Ruthenium dyes or 4T), porous TiO₂ (600 nm) / dye / P3HT ternary systems and the corresponding untreated porous TiO₂ (600 nm) / P3HT binary system and Figure 2 (b) shows the absorption spectra of corresponding dye in acetonitrile : tert-butanol (1:1 by volume) (0.06 mM). Although the peak absorbance of 4T dye solution is found at 470 nm²⁷, peak optical absorption of 4T dye treated porous TiO₂ (600 nm) film is shifted towards 440 nm, which suggests a disruption of the packing of 4T oligomers due to an interaction between 4T and the TiO₂ surface.

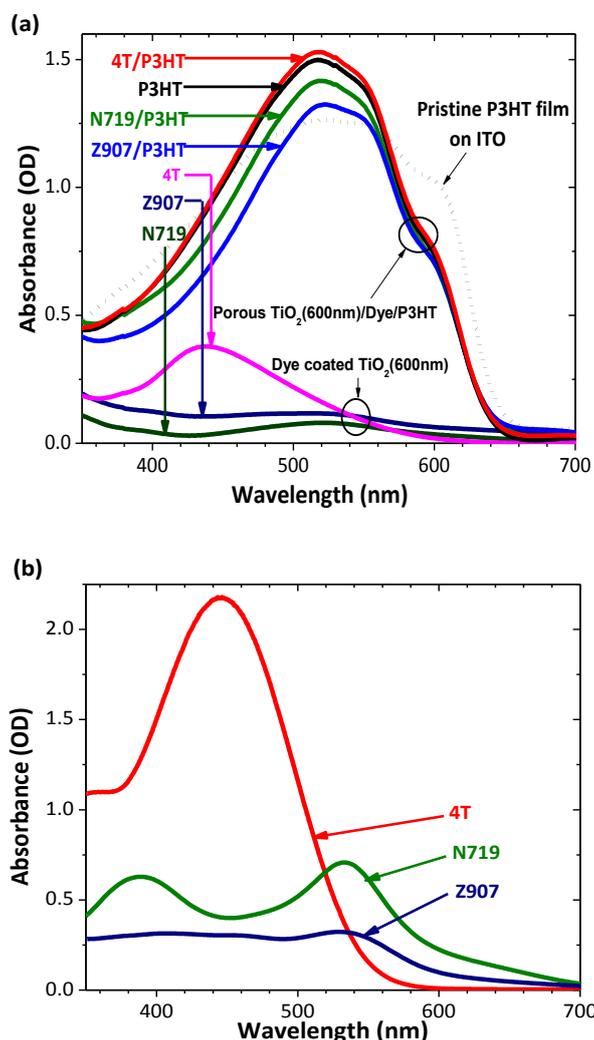


Figure 2. (a) Optical absorption spectra of porous TiO₂ (600 nm) / dye (Ruthenium dyes, 4T), porous TiO₂ (600 nm)/dye/P3HT ternary systems and the corresponding untreated porous TiO₂ (600 nm)/P3HT binary system and (b) absorption spectra of each of the three dyes in acetonitrile : tert-butanol (1:1 by volume) (0.06 mM).

The comparison of optical absorption spectra of porous TiO₂ (600 nm) / dye / P3HT ternary systems with its corresponding porous TiO₂ (600 nm) / dye binary system shows all dye coated TiO₂ films have weak absorption (OD~0.15) in comparison with absorption of TiO₂/ dye / P3HT films (OD~1.5) at the pumping wavelength of 532 nm though 4T treated porous TiO₂ films have significant absorption near to blue wavelength. It could also be clearly seen that the absorption spectra of untreated and treated films do not show any significant differences in their shape except a small increase or decrease in absorption. This indicates the microstructure of P3HT within a P3HT / TiO₂ composite is not strongly affected by the presence of these modifiers. However, comparison of absorption spectra for pristine P3HT and dye coated composites in Fig 2(a) shows that the packing of P3HT is apparently affected by the combination of the polymer with the TiO₂.

The sharper absorption edge in the red shown in the spectrum of pristine P3HT on ITO compared to those of the P3HT coated films (Figure 2(a)) suggest that the molecular packing of the polymer in the hybrid structures TiO₂ is disrupted somewhat relative to the pristine state.

In order to study the charge carrier mobilities in the composite samples, we used the time of flight (TOF) photocurrent technique to study samples of the structure ITO / Dense TiO₂ / active Layer / PEDOT:PSS / Au where the active layer is porous TiO₂ or TiO₂ / P3HT nanocomposite. In TOF, short laser pulses illuminate the sample through the TiO₂ electrode and so create a layer of electron-hole pairs in the polymer near the TiO₂ layers. The ITO is maintained either at positive potential for finding hole-mobility or at negative potential for electron mobility, such that charge carriers of sign opposite to that being studied are rapidly pulled towards the ITO / TiO₂ electrode, leaving the charge carriers of interest to drift across the samples towards the Au electrode under the influence of the electric field. The drifting photo-generated carriers then constitute an induced photocurrent transient which is analyzed to determine the charge transit time at that applied field and hence to find the electron or hole mobility in the composite film.

We study the following structures, (A) ITO / Dense TiO₂ / Porous TiO₂ (600 nm) / PEDOT:PSS / Au, (B) ITO / Dense TiO₂ / Porous TiO₂ (600 nm) / P3HT (250 nm) / PEDOT:PSS / Au, and (C) ITO / Dense TiO₂ / Porous TiO₂ (600 nm) / dye / P3HT (250 nm) / PEDOT:PSS / Au, using each of the three dyes. Here the dense TiO₂ and PEDOT:PSS layer serve as hole- and electron- blocking layers, respectively. Since the steady state absorption due to the dye in the nanocomposite at the pumping wavelength, 532 nm is significantly lower than the absorption of the porous TiO₂ / dye / P3HT nanocomposites (see Fig. 2 (b)), we can safely neglect the carrier generation in dye and its contribution to the charge transport in the active layer. Figure 2(a) confirms that all the samples are optically thick at the pumping wavelength of 532 nm, which is a necessary condition to determine carrier mobilities precisely by TOF.

The attempt to draw the hole in porous TiO₂ (structure A) by applying positive voltage to the illuminated transparent electrode was not successful even at very high voltage. This observation indicates that the hole-mobility of porous TiO₂ is very low. A photocurrent transient was observed when a

negative voltage was applied to the illuminated ITO. This photocurrent transient was assigned to electron transport.

Figure 3 (a) shows hole photocurrent transients at an applied field of $1.6 \times 10^{-5} \text{ V/m}$ for untreated ($\text{TiO}_2/\text{P3HT}$) (structure B) and treated structures ($\text{TiO}_2/\text{4T dye}/\text{P3HT}$) (structure C). Because of the absence of a hole photocurrent in structure A, we may safely assign the photocurrents in structures B and C to hole transport in the polymer phase. All transients are dispersive, possessing a monotonic decay with a change in gradient around a characteristic “knee” on a double logarithmic plot [Figure 3(a)]. Dispersive transport is typically assigned to trapping and de-trapping of charges from an energetic distribution of trap states during transit^{30,31,32}, and this is likely to be the reason for the dispersive transport in the case of these nanocomposites.

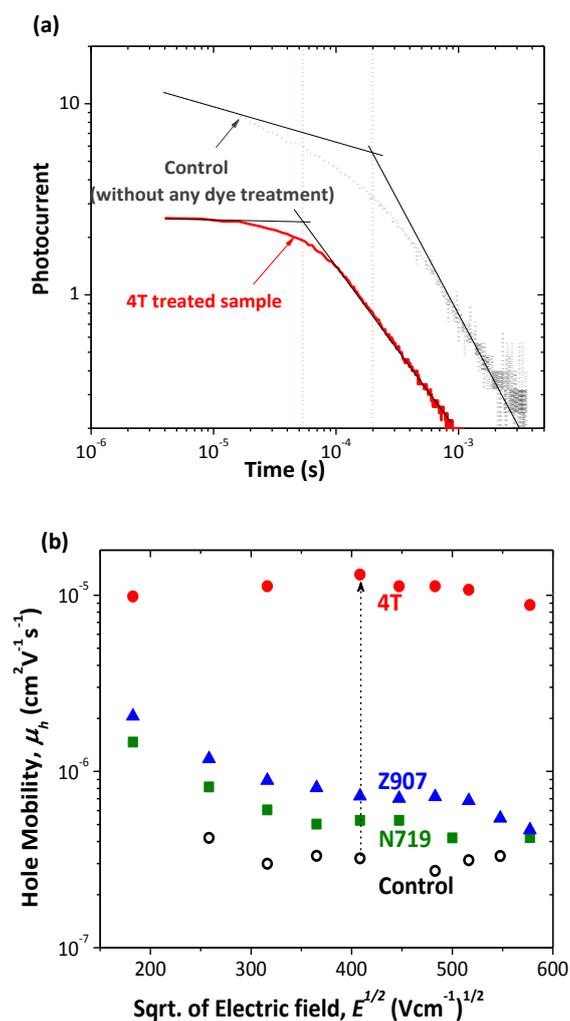


Figure 3. (a) The hole photocurrent transients at an applied field of $1.6 \times 10^{-5} \text{ V/m}$ for untreated ($\text{TiO}_2/\text{P3HT}$) (dashed line) and treated structures ($\text{TiO}_2/\text{4T dye}/\text{P3HT}$) (solid line) and (b) The electric-field dependence of drift mobility in $\text{TiO}_2/\text{P3HT}$ samples with and without interface modification. Filled circle for 4T, triangle for Z907, square for N719 treated films and open circle for $\text{TiO}_2/\text{P3HT}$ with no modifier (control).

Figure 3(a) shows that the hole-transient is around an order of magnitude faster in the 4T treated structure than the untreated one. Figure 3 (b) shows the hole mobility as a function of applied electric field for unmodified films and films modified with each of the three dyes. The hole mobility in the structure without dye interface layer is on the order of $10^{-7} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. This is comparable with reported values for some polymer / fullerene derivative devices obtained using TOF^{10,33} but is more than two orders of magnitude less than that of pristine P3HT where the hole-mobility has been reported as $3.0 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$.¹⁶ The poor hole transport may be due to disrupted packing of P3HT in the porous structure or to discontinuous pathways due to the TiO_2 mesostructure. However this poor hole mobility was increased by a factor of 2-5 when Ru based dyes were applied, and by over an order of magnitude when 4T was applied to the same porous TiO_2 matrix. Therefore the holetransport is influenced by the nature of the interface modifier and not only by the TiO_2 mesostructure. Figure 3 (b) also shows that only 4T treated films show more or less electric field independent mobility. Refer Figure 3 (d) in SI which compares time-of-flight profiles for 4T samples of two different thicknesses at the same applied electric field. The similar hole-mobility values in thin and thick samples support the assumption of uniform electric field and validate the TOF mobility values.

We now address the reasons for the higher hole-mobility in the dye treated, and particularly the 4T treated, composite films. One possible explanation is that the dye changes the surface energy of the TiO_2 surface to improve compatibility with P3HT and assist insertion of the polymer phase, which would lead to more continuous pathways for hole-transport¹ and so increase mobility. This idea is supported by measurements of the contact angle of water with the untreated and dye-treated TiO_2 surface shown in SI Fig. 5, which shows that the surface becomes much more hydrophobic upon dye treatment, and therefore more compatible with P3HT. There is no evidence from the optical absorption in Fig 2(a) to support a strong difference in polymer microstructure when using different dyes or no dyes, however, the composite absorption spectrum need not be correlated to pore penetration. Another effect of the dye layer could be to remove electrons by facilitating electron injection into the TiO_2 after exciton generation and so reduce the probability of hole recombination during transit. The LUMO energies of N719 and Z907 relative to P3HT^{34,1} would allow the dyes to serve as a shuttle for electron transfer to TiO_2 , and electron injection from these dyes into TiO_2 is known to be efficient.

Regarding the striking enhancement in hole-mobility of over an order of magnitude in 4T treated nanocomposite films compared to untreated films, we propose that this effect may be explained by the compatibility between the chemically similar P3HT and 4T chains, which is likely to lead to an attractive interaction between polymer and molecule. Such interaction between dissimilar thiophenes chains is analogous to the inter chain aggregation which is known to occur in P3HT polymer films and the aggregation within 4T in solution that was suggested by the spectra in Figure 2(a) and 2(b) above. This reasoning supports the idea that the 4T dye improves the penetration of polymer into pores of TiO_2 leading to a more continuous polymer phase for hole-transport than in the

absence of the dye. The higher hole-mobility is consistent with the higher photocurrent generation efficiency that is observed in TiO₂ / P3HT photovoltaic devices when the TiO₂ surface is coated with the respective dyes (SI Figure 4 (a) and (b)).

Conclusions

Hole-mobility improvements in hybrid TiO₂ / P3HT nanocomposites employing interface modifiers have been studied using the time-of-flight photocurrent technique. Hole mobility in the nanocomposite was improved by a factor of 2-5 relative to the unmodified TiO₂ / P3HT system when Ru based dyes (N719 and Z907) were introduced at the interface, and by over an order of magnitude when a quaterthiophene based dye (4T) was used. The strong effect of the 4T dye, which is chemically similar to the polymer, suggests that a dye-polymer interaction may assist in pore filling by the polymer and establish more continuous pathways for hole-transport. The hole mobility in the composite in the presence of the 4T dye is over 10⁻⁵cm²V⁻¹s⁻¹ which is only an order of magnitude smaller than that in pristine P3HT polymer. Dyes may also assist hole-transport by facilitating electron injection into the TiO₂ and reducing hole loss by recombination. Further studies are needed to clarify the mechanism of improved hole-transport. We conclude that interface modification using carefully chosen dyes may significantly improve hole-mobility in Hybrid TiO₂ / P3HT nanocomposites.

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Notes and references

Author Contributions

K.P. and P.R. designed and organized the project, developed interpretation of the results and wrote the manuscript. K.P. and T.T. fabricated the solar cell devices, carried out optical and electrical characterizations, TOF experiments and data analysis. M.P. and N.R. carried out the synthesis and design of the 4T polymer. P.R., N.R. and J.N. developed the interpretation of the results and supported the writing of the manuscript.

‡ ESI is available for this manuscript.

1. P. Ravirajan, et al., *The Journal of Physical Chemistry B*, 2006, **110**, 7635-7639.
2. M. He, F. Qiu, and Z. Lin, *The journal of physical chemistry letters*, 2013, **4**, 1788-1796.
3. Z. Wang, et al., *Applied Surface Science*, 2008, **255**, 1916-1920.

4. J. Weickert, et al., *The Journal of Physical Chemistry C*, 2011, **115**, 15081-15088.
5. P. Atienzar, et al., *The Journal of Physical Chemistry Letters*, 2010, **1**, 708-713.
6. P. Ravirajan, et al., *Thin Solid Films*, 2004, **451**, 624-629.
7. B.O. Aduda, et al., *International Journal of Photoenergy*, 2004, **6**, 141-147.
8. J. Nelson, *Physical Review B*, 1999, **59**, 15374.
9. J. Nelson, J. Kirkpatrick, and P. Ravirajan, *Physical Review B*, 2004, **69**, 035337.
10. S. Choulis, et al., *Applied physics letters*, 2003, **83**, 3812-3814.
11. R. Mauer, M. Kastler, and F. Laquai, *Advanced Functional Materials*, 2010, **20**, 2085-2092.
12. K. Yang, et al., *Journal of Macromolecular Science, Part A*, 2007, **44**, 1261-1264.
13. D. Poplavskyy and J. Nelson, *Journal of Applied Physics*, 2003, **93**, 341-346.
14. P. Ravirajan, et al., *Advanced Functional Materials*, 2005, **15**, 609-618.
15. T. Yoshikawa, et al., *Thin Solid Films*, 2008, **516**, 2595-2599.
16. S. Choulis, et al., *Applied physics letters*, 2004, **85**, 3890-3892.
17. M. Thanishaichelvan, et al., *Journal of Materials Science: Materials in Electronics*, 2015, **26**, 3558-3563.
18. K.M. Coakley, et al., *Advanced Functional Materials*, 2005, **15**, 1927-1932.
19. S. Loheeswaran, et al., *Journal of Nanoelectronics and Optoelectronics*, 2013, **8**, 484-488.
20. E. Palomares, et al., *Journal of the American Chemical Society*, 2003, **125**, 475-482.
21. Y. Hu, et al., *Journal of Materials Chemistry A*, 2016, **4**, 2509-2516.
22. A. Abate, et al., *Advanced Energy Materials*, 2014, **4**.
23. S. Loheeswaran, et al., *Journal of Materials Science: Materials in Electronics*, 1-6.
24. D. Moia, et al., *Advanced Materials*, 2015, **27**, 5889-5894.
25. D. Moia, et al., *The Journal of Physical Chemistry C*, 2015, **119**, 18975-18985.
26. R.A. Krüger, et al., *ACS applied materials & interfaces*, 2011, **3**, 2031-2041.
27. M. Planells, et al., *ACS applied materials & interfaces*, 2014, **6**, 17226-17235.
28. P. Ravirajan, et al., *Journal of applied physics*, 2004, **95**, 1473-1480.
29. S. Rutledge and A. Helmy, *Journal of Applied Physics*, 2013, **114**, 133708.
30. B.C. O'Regan and J.R. Durrant, *The Journal of Physical Chemistry B*, 2006, **110**, 8544-8547.
31. A. Janotti, et al., *Physical Review B*, 2010, **81**, 085212.
32. J. Varley, et al., *Physical Review B*, 2012, **85**, 081109.
33. V.D. Mihailetschi, et al., *Advanced Functional Materials*, 2006, **16**, 699-708.
34. I. Chung, et al., *Nature*, 2012, **485**, 486-489.