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Effect of Interface Modifiers on Hole Mobility in Hybrid Nanoporous Titanium dioxide (TiO₂) / Poly(3-hexylthiophene) (P3HT) Solar Cells

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Abstract—This study focuses on influence of interface modifiers on hole mobility in Hybrid Nanoporous Titanium dioxide (TiO₂) / Poly(3-hexylthiophene) (P3HT) nanocomposite by using time of flight technique. We found that the hole-mobility in the composite material is more than two orders of magnitude less than that of pristine P3HT. This may be due to poor polymer infiltration of the polymer into highly structured porous TiO₂. However, hole-mobility of the polymer in TiO₂:P3HT is increased to an order of magnitude when ruthenium based dye either Z907 or N719 is introduced at the TiO₂/P3HT interface. This is consistent with corresponding current density (J) – voltage (V) charateristics of thin TiO₂ / P3HT devices with or without dye interface layer. Better JV characteristics of the device and higher hole mobility of P3HT found in TiO₂ / dye / P3HT may be due to passivation of surface traps by the dye.

Keywords - Time of Flight, P3HT, Hybrid Solar Cell, CarrierMobility

I. INTRODUCTION

Organic devices based on TiO₂:P3HT films are attracting extensive interest due to their high mechanical stability and the multiple routes available to control the interface morphology incorporated with good electron transport property of TiO₂ electron acceptor.

However performance improvements are needed to develop high power conversion efficiency devices, which have been mainly limited due to poor infiltration of polymer into porous TiO₂ and poor charge transport in TiO₂/polymer nanocomposite, through understanding the underlying charge transport properties in the as stated molecular structure. Although a few independent studies had been reported to find the electron mobility in porous TiO₂ [1] and hole mobility in poly(3-hexylthiophene) (P3HT) [2], no successful study on charge transport in TiO₂/polymer composite materials has been reported by employing Time of Flight (TOF) technique. Several techniques have been used in addition to modifying the metal oxide surface using thin molecular layer to improve the

hole mobility in hybrid structures including controlling polymer alignment to enhance the overall device performance [3]. Recently it has also been reported that the thin layer of alumina reduces the recombination kinetics of the TiO₂-P3HT solar cells and thus improves the overall performance of the device [4]. This work focuses on effects caused on hole mobility in Hybrid Nanoporous Titanium dioxide (TiO₂) / Poly(3-hexylthiophene) (P3HT) nanocomposite when ruthenium based dyes Z907 and N719 act as interface modifiers using time of flight technique.

II. EXPERIMENTAL PROCEDURE

A. Fabrication of solar cell

Samples were prepared on patterned Indium Tin Oxide (ITO) coated glass substrates (12 mm × 12 mm, 10 Ω/square), which were cleaned similar to those reported elsewhere [5]. A dense hole blocking layer was deposited by spray pyrolysis. In order to deposit the electron transporting layer of about 600 nm porous nanocrystalline TiO₂, ITO substrates were spun coated by TiO₂ paste (DSL 18NRT, Dyesol) dissolved in tetrahydrofuran (THF).

Thin layer of Z907 and N719 were deposited by dip coating and then the samples were dipped in P3HT overnight prior to P3HT spin coating. Subsequently these samples were precoated with Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) before depositing top contactof 40 nm Au by thermal evaporationthrough a shadow mask under high vacuum. Finally silver paste was applied and annealed to improve the contacts during measurements.

B. Characterization techniques

The carriers were generated with a frequency-doubled Nd:YAG laser (spectral wavelength 532 nm, pulse width less

than 6 ns, energy per pulse ~ 10 mJ, 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) while ITO terminal with positive potential. The optical absorption spectra of thin layers of Z907 and N719 coated nanoporous TiO_2 electrodes and a spectrum of dip and spin coated P3HT onto both Z907 and N719 treated TiO_2 samples were obtained by using UV-Vis spectrometer (JENWAY-6800).

III. RESULTS AND DISCUSSION

Fig.1 shows both Ruthenium based dyes coated TiO_2 films have low absorption in the visible region, 532 nm in particular they possesses little absorption near to lasing wavelength of 532 nm, which cannot be overlooked. While the absorption of dip and spin coated P3HT film onto Ruthenium based dye treated TiO_2 has very high absorption in the visible region, 532 nm in particular, and this effect could be attributed to the high absorption coefficient of P3HT hole conductor. Since the thickness of these modifiers have been limited to very thin ($\ll$ absorption depth δ of the laser used) and the samples were lased at 532 nm any observable features in hole transport could be addressed by the improved interconnected pathways between P3HT and TiO_2 while modifiers are present and the contribution from the modifiers can easily be eradicated.
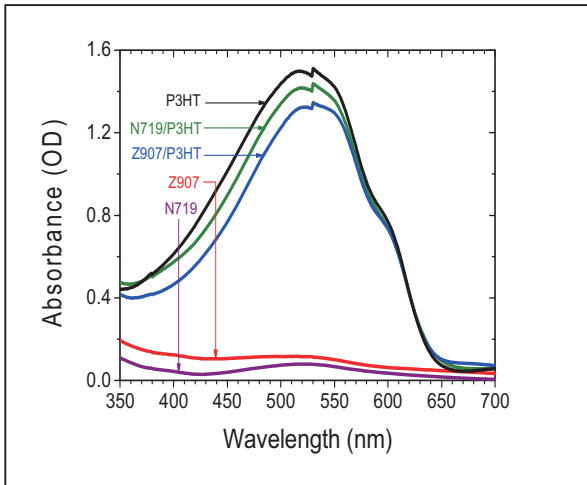

Fig. 1. Optical absorption spectra of Ruthenium based dyes coated TiO_2 films and dip and spin coated P3HT onto Ruthenium based dyes treated TiO_2 films with spectrum of bare P3HT.

Fig. 2 shows typical photocurrent transients with varying applied bias voltage for (a) bare TiO_2:P3HT and (b) Z907 modifier coated TiO_2:P3HT structures. The photocurrent transients are dispersive, possessing a decay with a characteristic ''knee'' on a double logarithmic plot. Dispersive transport is an indication of disorder, which may be due to trap states in the hole transporting polymer. We found that the hole-mobility in the composite material is in the order of $10^{-7} cm^2 V^{-1} s^{-1}$. But in pristine P3HT the hole mobility at
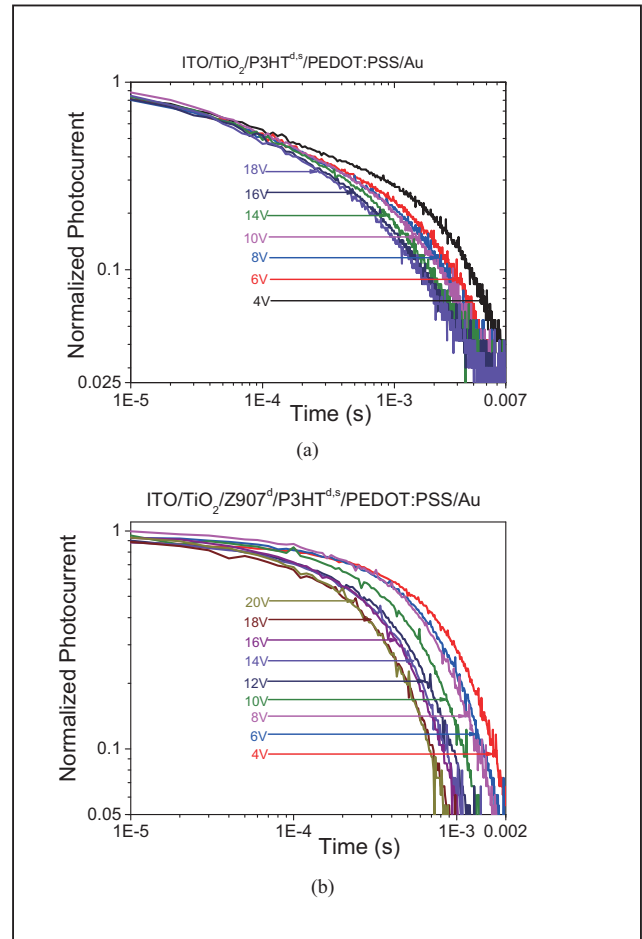

Fig. 2. Typical TOF hole transients as a function of voltage for (a) untreated TiO_2:P3HT films and (b) Z907 dye treated TiO_2:P3HT films.

2.5×10^5 Vcm^{-1} was reported as $3.0 \times 10^{-4} cm^2 V^{-1} s^{-1}$ [2]. Therefore the value we found is more than two orders of magnitude less than that of pristine P3HT. The poor hole transport may be due to poor interconnected pathways between TiO_2/P3HT interfaces apart from the poor hole mobility in TiO_2. However this poor hole mobility was increased to an order when ruthenium based dyes were applied.

It is also noticeable that all these variations do not obey the Poole-Frenkel dependence $\left(\mu = \mu_0 exp\left(\beta E^{1/2} \right) \right)$ and showed a negative field-dependent mobility at low fields and this results are consistent with the model developed by Takashima et al. [6] for poly(alkylthiophene) polymers.

According to Takashima et al. model the relationship between the transit time t_r and the carrier mobility μ can be written as

$$t_r V_a = \Psi V_a^{1/2} + l^2 / \mu$$

Here Ψ is a constant given by $\Psi = \frac{\sigma_b l}{\sigma_d}\left(\frac{2\varepsilon\varepsilon_0}{en_0}\right)^{1/2}$ where σ_d conductivity of depleted region, σ_b conductivity of undepleted bulk region, l sample thickness, ε dielectric permittivity, ε_0 permittivity of free space, e electronic charge and n_0 equilibrium carrier density and V_a applied bias voltage. As shown in Fig. 3 our results are best fitted with this equation and the values found from the intercept for the mobilities are comparable to those obatained from $\mu = \frac{l^2}{V_a t_r}$
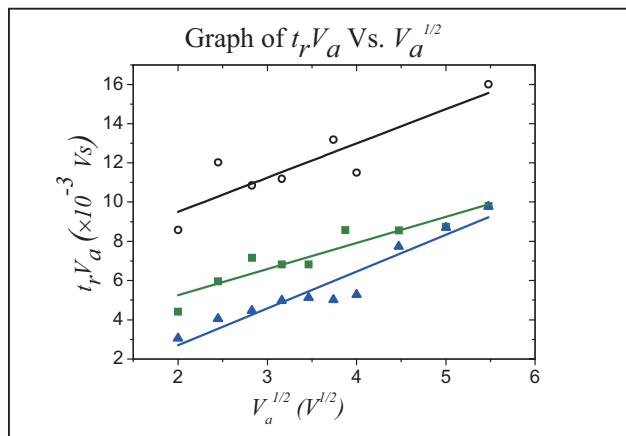

Fig. 3. The plot of transit time t_r multiplied by applied bias voltage V_a versus square root of applied bias voltage for bare TiO$_2$ (open circles) based device and N719 (filled squares) and Z907 (filled triangles) coated TiO$_2$ films based devices.

From the above graph we found the hole mobility in TiO$_2$/P3HT nanocomposites with and without interface modifiers and the values clearly show that dyes improve the charge transport of P3HT. Hole mobility found in TiO$_2$/N719/P3HT and TiO$_2$/Z907/P3HT is about an order of magnitude greater than in TiO$_2$/P3HT (without dye).This is consistent with JV data. Hole mobility in TiO$_2$/P3HT can be improved by introducing Ruthenium based dyes as interfacial layer.

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