Effects of Carrier Mobility on Photocurrent Generation in TiO₂/Poly(alkylthiophene) Photovoltaic Devices

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Abstract: In heterojunction photovoltaic devices of ITO/TiO₂/poly(3-alkylthiophene)/Au, the photocurrent was characterized at different temperatures for different alkyl chain lengths and regioregularities: regiorandom, regioregular poly(3-hexylthiophene), and regioregular poly(3-dodecylthiophene). The regioregularity and alkyl chain length affected the photovoltaic characteristics due to differences in hole-carrier transportation. The drift charge mobilities of these devices were analyzed by the space-charge-limited current theory using the relation between the dark current and the bias voltage. The photocurrent in the devices based on poly(3-alkylthiophene)s decreased rapidly below the temperature at which the drift charge mobility was 10^{-5} cm²/V · s.

Keywords: poly(3-alkylthiophene), charge mobility, photovoltaics, heterojunction.

Introduction

Organic semiconducting materials are used in diverse applications, such as solar cells,[1] organic light-emitting diodes,[2] and organic thin-film transistors.[3] Among the various electrically conducting polymers, poly(3-alkylthiophene)s (PATs) can be made soluble by substituting long alkyl chains or functional groups[4] at the 3 position, and their polymerization can be controlled by the coupling at the head and tail. The thus-obtained regioregular head-tail PATs are expected to show high mobility.[5]

In this study, three PATs with different alkyl chain lengths and regioregularities - regioregular poly(3-hexylthiophene) (RP3HT), regioregular poly(3-dodecylthiophene) (RP3DT), and regiorandom poly(3-hexylthiophene) (P3HT) - were used as hole conductors to investigate the structure and property relationships on photocurrent generation in terms of carrier mobility at different temperatures.

Illumination of a photovoltaic device of indium-tin oxide (ITO)/TiO₂/PAT/Au results in charge separation at the interface between TiO₂ after excitons are generated in the conjugated polymer. In the short-circuit condition, excited electrons are injected into TiO₂ on a femtosecond timescale due to the energy difference between the lowest unoccupied molecular orbital level of PAT (-2.9 eV) and the quasi-Fermi level of

TiO₂ (-4.2 eV), whereas holes move toward the Au electrode through the PAT layer in the opposite direction. The photocurrent is delivered to a load by draining the hole carriers to the back contact. The electron mobility through TiO₂ in the conjugated polymers is several orders of magnitude faster than the hole mobility, and hence the hole mobility is one of the most important parameters for achieving high-performance polymer photovoltaics. Several groups have reported temperature-dependent photovoltaic characteristics in organic bulk heterojunction solar cells.[6-8] In the present study, we found that the photocurrent generation in TiO₂/PAT devices was strongly affected by the charge-carrier mobility around the critical value of 10^{-5} cm²/V · s.

Experimental

Photovoltaic cells were fabricated with a multilayered structure using heterojunctions of inorganic TiO₂ and an organic polymer layer. The TiO₂ layer was spin coated onto ITO-coated glass substrates from a sol-gel solution of titanium isopropoxide in ethanol, and then annealed for 30 min at 450 °C in air.[9] The thickness of the TiO₂ layer was approximately 30 nm after calcination. The device with mesoporous nanocrystalline TiO₂ particles demonstrated conversion efficiencies of about 1.5% under monochromatic illumination at 514 nm and of 0.45% for AM1.5 illumination.[10] However, we used a compact TiO₂ layer from the sol-gel precursor since

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the air remaining in the pores in mesoporous TiO$_2$ particles resulted in a delamination problem between the polymer layer and TiO$_2$ surface under a vacuum condition of less than 10^{-3} torr for the low-temperature measurements in a cryostat. The P3HT (M_w = 120,000 g/mol) was polymerized with FeCl$_3$ oxidant,[11] and the RP3HT (M_w = 87,000 g/mol) and RP3DT (M_w = 162,000 g/mol) were purchased from Aldrich Co. and used after reprecipitation from a chloroform solution. The polymer layers were spin coated from a mono-chlorobenzene solution to a thickness of 500 nm as measured using a surface profiler (P-10, Tencor). The Au layer for the back contact electrode was evaporated thermally on the polymer film at below 10^{-5} torr.

The typical active area of the photovoltaic device was 0.18 cm^2. The current density-voltage (J-V) characteristics were obtained with a source measure unit (Keithley 236) placed across the ITO (negative) and Au (positive) electrodes under radiation from a 300-W Xe arc lamp (Oriel) passed through a global AM1.5 solar-simulating filter. The incident photon-to-electron conversion efficiency (IPCE) was measured using a photon-counting spectrofluorometer (ISS PC1) equipped with a 350-W Xe arc lamp and a motorized mono-chromator. The incident light intensity was calibrated using a photodiode detector (Newport 818UV) and an optical power meter (Newport 1830-C). J-V characteristics at low temperatures were measured in a helium-circulated cryostat (JANIS) in the temperature range from 100 to 300 K.

Results and Discussion

The regioregular and random PAT structures are presented in Figure 1. The alkylthiophene monomeric units are connected as a head-to-tail formation in regioregular polymers and are randomly sequenced in regiorandom polymers. The normalized absorption spectra of RP3HT, RP3DT, and P3HT films are shown in Figure 2(a). The peaks in the RP3HT and RP3DT spectra are red-shifted to a longer wavelength compared to that in the P3HT spectrum due to the long conjugation length as expected in the regioregular configuration. The vibronic structures are also observed clearly in the RP3HT and RP3DT spectra.

The monochromatic IPCE, defined as the number of electrons generated by light in the external circuit divided by the
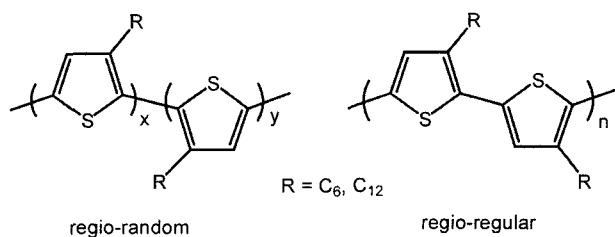
number of incident photons, is plotted in Figure 2(b) as a function of the excitation wavelength. This was derived from the photocurrents using,

$$IPCE(\lambda)[\ \%] = \frac{1240 \times J_{sc}(\lambda)[\mu A/cm^2]}{\lambda[nm] \times P[W/m^2]} \times 100 \qquad (1)$$

where λ is the wavelength, $J_{sc}(\lambda)$ is the short-circuit photocurrent density under monochromatic illumination, and P is the power of the incident light.

The IPCE spectra of the ITO/TiO$_2$/RP3DT/Au device are shown in Figure 2(b). The symbatic correlation in the visible range between the photocurrent spectrum and the absorption spectrum implies that the active interface for charge-carrier generation in the device is the RP3DT/TiO$_2$ interface as a result of the formation of singlet excitons in RP3DT. The number of excitons generated was considered to be independent of temperature, given that the absorbance spectra at low temperatures were similar to those at 300 K. TiO$_2$ also contributes to the photocurrents in the UV range due to the energy-band gap of TiO$_2$. In IPCE spectra, the contribution
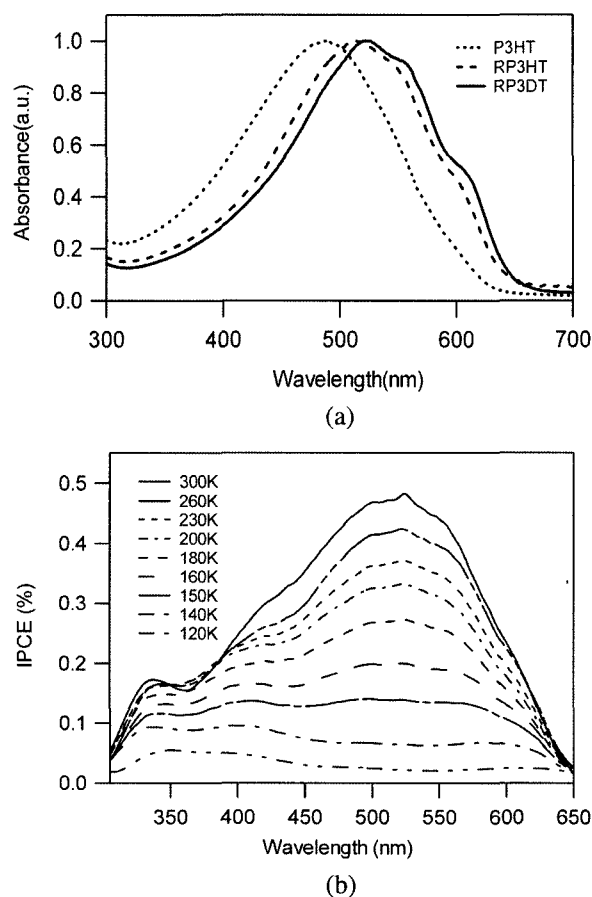

(a)

(b)

Figure 2. The UV-Vis spectra of P3HT, RP3DT and RP3HT films (a) and the IPCE spectra of ITO/TiO$_2$/RP3DT/Au device at different temperatures (b).
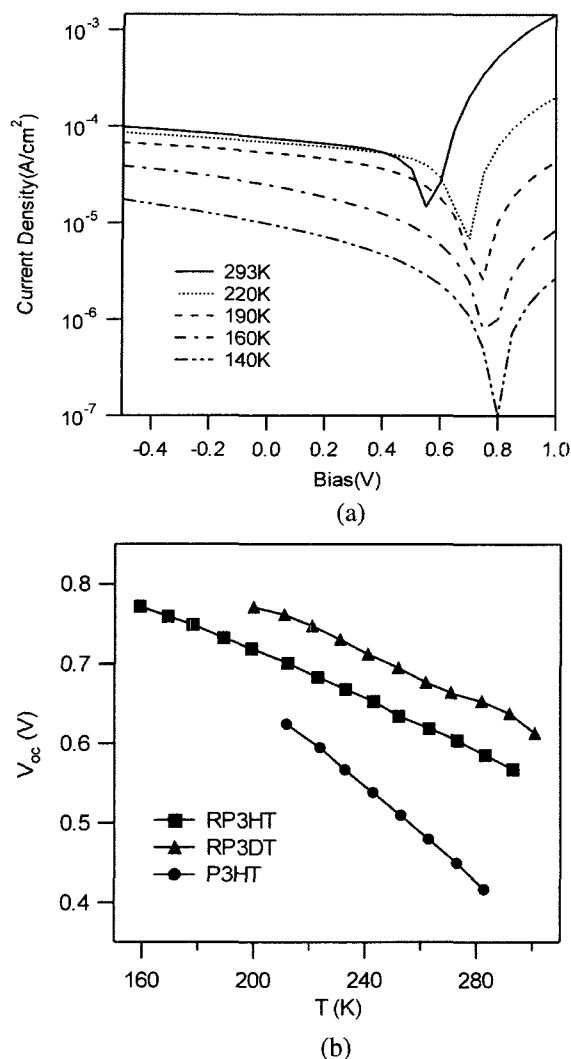

R = C$_6$, C$_{12}$

regio-random   regio-regular

Figure 1. Chemical structures of regio-random (left) and regular (right) PATs.

(a)

(b)

Figure 3. The J-V characteristics of ITO/TiO$_2$/RP3HT/Au device at different temperatures (a) and the temperature dependence of V_{oc} (b).

of RP3DT in the visible range decreases significantly at low temperatures compared to those of the TiO$_2$ layer due to difficulties in hole-carrier transport.

The J-V characteristics of ITO/TiO$_2$/RP3HT/Au devices were measured at different temperatures under 50 mW/cm^2 illumination (Figure 3(a)). The photocurrent density decreased gradually as the temperature decreased. On the other hand, the open-circuit voltage (V_{oc}) increased almost linearly as the temperature decreased from 300 to 180 K (Figure 3(b)). We use the following model for conventional inorganic semiconductor solar cells to explain the obtained characteristics of V_{oc},[12]

$$V_{oc} = \frac{E_g}{q} - \frac{kT}{q}\ln\left[\left(\frac{D}{\tau}\right)^{1/2} T^3 \frac{B}{J_{sc}}\right] \tag{2}$$

where E_g is the band-gap energy (eV), q is the electron charge (1.6×10^{-19} C), k is Boltzmann's constant, T is the absolute temperature, D is the diffusion coefficient (cm^2/sec), and τ is the minority-carrier lifetime. The variation in V_{oc} with temperature is often used to estimate the effective barrier height for experimental photovoltaics. Its extrapolation to $T = 0$ K yields the maximum theoretical V_{oc} for photovoltaics, $V_{oc}(0)$, which was 1.09, 1.02, and 1.25 V for RP3DT, RP3HT, and P3HT, respectively. $V_{oc}(0)$ is related to the difference between the conduction band of TiO$_2$ (-4.2 eV) and the highest occupied molecular orbital level of typical PATs (-5.2 eV) in ITO/TiO$_2$/PAT/Au devices.

The short-circuit currents (J_{sc}) of those polymers at different temperatures are shown in Figure 4, with the normalized values for RP3HT, RP3DT, and P3HT shown in the Figure inset. The J_{sc} decreased gradually with decreasing temperature in the PAT devices. The J_{sc} values at room temperature were 0.075, 0.045, and 0.038 mA/cm^2 for RP3HT, RP3DT, and R3HT, respectively. The normalized J_{sc} curves exhibit a sigmoidal relation versus temperature. However, each polymer shows a different critical temperature (T_c), defined as the temperature at which the J_{sc} rapidly decreases. In polymeric heterojunction photovoltaics, the photocurrent depends on the charge transport efficiency of hole carriers to the Au electrode.

In this study, the charge mobility was estimated according to the space-charge-limited current (SCLC) theory using the dark-current J-V characteristics, which were typical Schottky-type behaviors. One method for determining charge-carrier mobilities is to examine the SCLC through a semiconductor in the dark, since it is directly proportional to the charge-carrier mobility,[13]

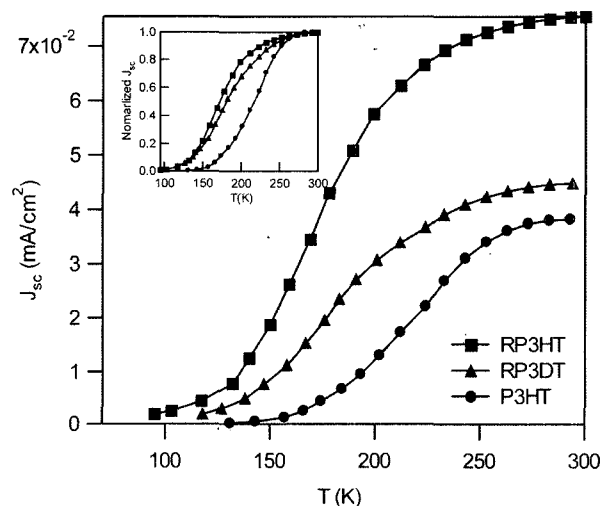$$J = \frac{9}{8}\varepsilon_o\varepsilon_r\mu\frac{V^2}{d^3} \tag{3}$$

Figure 4. The short-circuit current density of P3HT, RP3HT, and RP3DT devices at different temperatures and the normalized short-circuit current density (inset).

where J, ε_o, ε_r, V, d, and μ are the dark-current density, permittivity constant, permittivity, bias voltage, device thickness, and drift charge mobility, respectively.

In SCLC theory, the current is proportional to the square of the applied bias in a trap-filled condition. The drift charge mobility is estimated from the J-V characteristics in the dark condition from the slope of J versus V^2: in RP3HT, RP3DT, and P3HT it was 2.64×10^{-4}, 1.47×10^{-4}, and 3.46×10^{-5} cm²/V·s, respectively, at 300 K, and decreased with decreasing temperature (Figure 5). The regioregular structure of PAT enhances the charge-carrier mobility compared to that of regiorandom types due to a longer conjugation length, as shown in Figure 2(a). However, the long alkyl side chains interrupt the carrier migration between π-conjugated main chains in 3-alkyl-substituted PATs.[14] The value of T_c is related to the drift charge mobility, and was 223, 233, and 273 K for RP3HT, RP3DT, and P3HT, respectively, from the normalized J_{sc}, and the drift mobility was 5.4×10^{-5}, 4.8×10^{-5}, and 1.8×10^{-5} cm²/V·s. A mobility of 10^{-5} cm²/V·s was found to be a critical value for the efficient photogenerated carrier transport in photovoltaic devices based on PATs.

We have presented the structure and property relations in heterojunction photovoltaics based on PATs with a TiO₂ layer. The regioregularity and alkyl chain length affect the
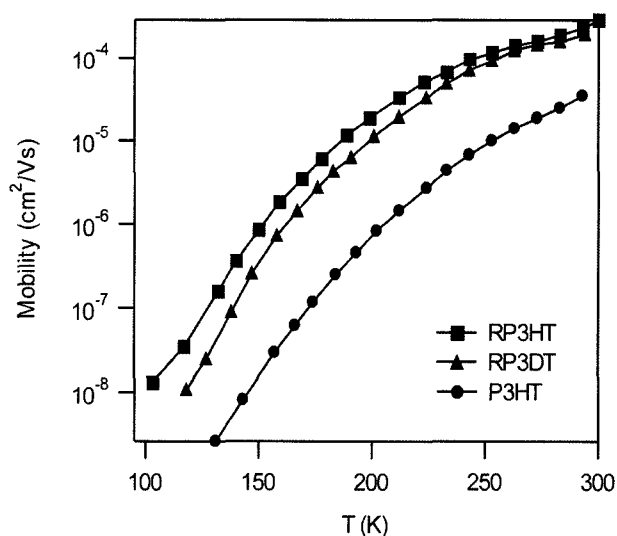
photocurrent generation of the devices. PATs contribute to the photocurrent as sensitizers and hole-transporting materials from the symbatic correlation between the absorbance and IPCE spectra. The temperature dependence of J_{sc} was dominated by the charge mobility of hole carriers as analyzed by the SCLC theory. Regioregular types of PAT (RP3HT and RP3DT) showed a larger photocurrent and lower T_c than the regiorandom P3HT due to the faster charge mobility.

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Figure 5. Hole carrier mobility of PATs calculated from the SCLC theory at different temperatures.