

Method for increasing the photoconductive response in conjugated polymer/fullerene composites

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The authors poly(3-hexylthiophene)/[6,6]-phenyl C61-butyric acid methyl ester present a technique for modifying the internal structure of bulk heterojunction films which yields significantly improved photoconductivity. This method comprises the addition of alkyl thiol molecules to the polymer/fullerene solution prior to spin coating. Based on the steady-state and transient photoconductivity measurements, the photoresponsivity is an order of magnitude greater than that in films spun from pristine solvent; additionally, the carrier mobility measurements indicate significant increase in the hole mobility, consistent with the enhanced structural order inferred from x-ray diffraction and optical absorption measurements. © 2006 American Institute of Physics. [DOI: 10.1063/1.2408661]

Bulk heterojunction (BHJ) blends containing a conjugated polymer and fullerene derivatives have the potential to be utilized as inexpensive, flexible, photoconductive devices such as photodetectors and solar cells.¹⁻³ BHJ solar cells containing regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) have demonstrated power conversion efficiencies as high as 5%.¹ In BHJ systems, absorption of incident light generates free carriers and bound electron-hole pairs (excitons) in the polymer;^{1,4} an ultrafast charge transfer reaction from the polymer donor to the fullerene acceptor dissociates the excitons and thus significantly increases the density of mobile carriers and thereby enhances the photoconductive response.^{1,5,6}

Recent advances in P3HT/PCBM solar cells demonstrate that controlling the rate of solvent evaporation during spin coating and thermal annealing of the devices after the deposition of the cathode increases structural order in the P3HT domains, resulting in improved device efficiency and charge transport characteristics.^{1,7-9} While investigating the incorporation of gold nanoparticles into P3HT/PCBM films, we found that the presence of excess surfactant had a dramatic effect on film morphology. Measurements of steady-state and transient photoconductivities, thin film transistor (TFT) mobility, optical transmission, and x-ray diffraction demonstrate that the incorporation of short-chain alkyl thiols in the casting solution markedly enhances the photoconductive response of the resulting films due to increased structural order.

Films for photoconductivity (PC) measurements were spun at 700 rpm from a 10:8 mg/mL ratio of P3HT:PCBM in toluene on alumina substrates, while the films for x-ray diffraction and optical transmission were spun on glass substrates. TFT devices were spun at 2000 rpm on heavily doped *n*-type Si coated with a 200 nm silica dielectric layer treated with octyltrichlorosilane. The source and drain electrodes comprised of 50 nm thick Au deposited on a 5 nm thick Ti adhesion layer in a bottom contact geometry; the

TFT channel lengths were 5 or 10 μm and the channel width was 1 mm.^{7,10} The photoconductive response (R), in terms of photocurrent per incident light power (A/W), was measured using an external field of $F=5$ KV/cm. For the steady-state and transient photoconductivity measurements we employed a standard modulation technique¹¹ and an Auston switch sample configuration, respectively.¹²

BHJ is used in this letter to abbreviate P3HT/PCBM films. BHJ is followed by labels for the alkyl thiol concentration in the casting solution (if any), the alkyl chain length, and the thermal history. Annealing at 150 °C for 15 min is indicated by an “A” (or “NA” in the absence of annealing). For example, BHJ-1%C8-A corresponds to a thermally treated film prepared from a toluene solution containing 1% *n*-octylthiol.

The photoconductivity (σ) is defined by Eq. (1), where e is the electron charge, n the number of either electrons or holes, μ the carrier mobility, and τ the carrier lifetime,^{5,6}

$$\sigma = e[(n_h \mu_h \tau_h) + (n_e \mu_e \tau_e)]. \quad (1)$$

Steady-state PC measurements were performed on films as a function of annealing [Fig. 1(a)], alkyl chain length [Fig. 1(b)], and alkyl thiol concentration [Fig. 1(c)]. Note that the sharp peaks in the spectra are artifacts due to filter changes. Figure 1(a) shows that, while annealing increases the responsivity of BHJ-NA by a factor of 6,^{13,14} inclusion of 5% *n*-octylthiol in the polymer solution combined with the thermal annealing increases the responsivity by a factor of 60. Figure 1(b) shows that utilizing *n*-octylthiol results in higher responsivity than *n*-dodecylthiol or *n*-hexylthiol; Figure 1(c) indicates that among the concentrations of *n*-octylthiol tested, the sample obtained from a 5% by volume solution exhibited the highest responsivity.

From the maximum responsivity measured in BHJ-5%C8-A at 590 nm, and taking into account the sample cross sectional area of 6×10^{-7} cm², we estimate a photocurrent density per watt of incident radiation of $J=4 \times 10^5$ A/cm². This magnitude of J corresponds to high photoconductivity of $\sigma=200$ S/cm at $E=5$ KV/cm.

TFT devices processed from 5% alkyl thiol in toluene demonstrated a significant increase in the hole mobility from $2.7 \times 10^{-4} \pm 1.5 \times 10^{-4}$ to $1.63 \times 10^{-2} \pm 5.7 \times 10^{-3}$ cm²/V s.

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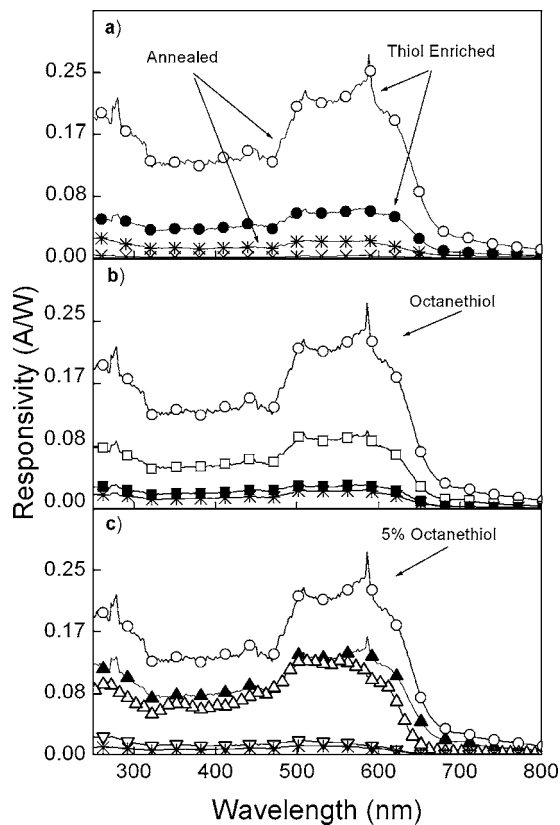


FIG. 1. Effect on photoconductivity of (a) annealing and enrichment with 5% *n*-octanethiol, (b) alkyl thiol chain length, and (c) *n*-octylthiol concentration. Samples are on alumina substrates and consist of: BHJ-NA (×), BHJ-A (*), BHJ-5%C8-A (○), BHJ-5%C8-NA (●), BHJ-5%C12-A (■), BHJ-5%C6-A (□), BHJ-0.1%C8-A (▽), BHJ-1%C8-A (△), and BHJ-10%C8-A (▲).

Annealing of the films processed with alkyl thiol leads to a further increase in the mobility to $3.9 \times 10^{-2} \pm 6.5 \times 10^{-3}$. Mobilities were calculated from the transconductance characteristics (seen in Fig. 2) using a linear regression of the $I_d^{1/2}$ vs V_g at a fixed V_d of -100 V, where I_d is the drain-source current and V_g and V_d are the gate and drain voltages, respectively.¹⁵

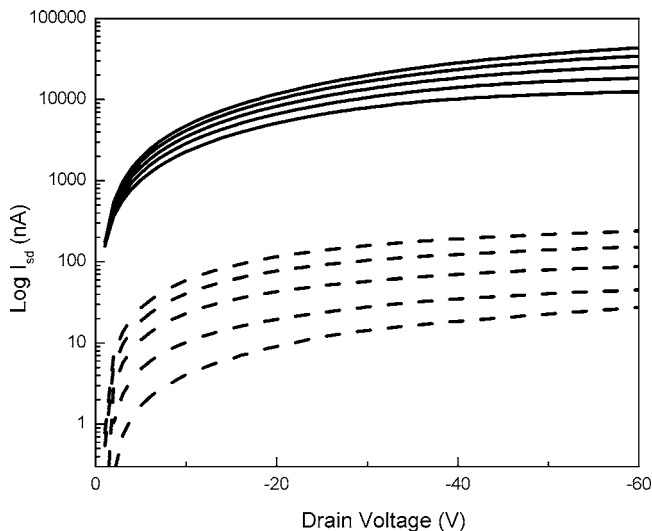


FIG. 2. Transistor behavior of films in log scale: BHJ-NA (dashed line) and BHJ-5%C8-NA (solid line) at gate voltages of 0, -7.5 , -15 , -22.5 , and -30 V.

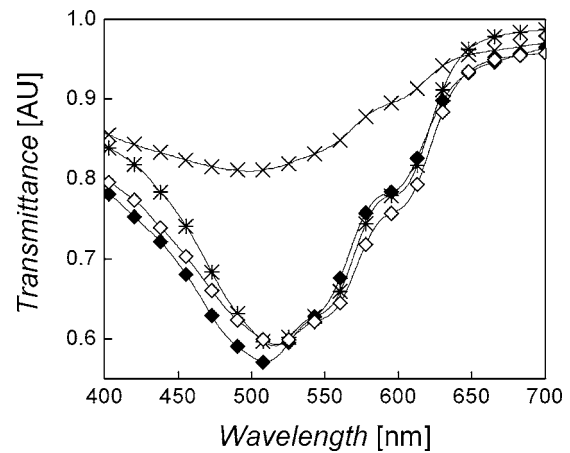


FIG. 3. Transmittance through films for films on glass substrates: BHJ-NA (×), BHJ-A (*), BHJ-1%C8-NA (◆), and BHJ-1%C8-A (◇).

Figure 3 compares the optical transmittance of films processed with and without alkyl thiol molecules. As is evident from the data, the incorporation of *n*-octylthiol (between 0.1% and 10% by volume) decreases the optical transmittance similarly to the effect seen due to thermal treatment.^{7,8} The increase and redshift in absorption combined with the appearance of vibronic replica in the absorption spectra indicated the presence of crystalline P3HT domains.¹³

This technique has also been demonstrated to decrease optical transmittance prior to annealing when used with a variety of solvents including chlorobenzene, dichlorobenzene, and chloroform and with a variety of alkyl containing additives such as octanol, undecane, and phenyl octane. The independence of the increased absorption on solvent boiling point or additive polarity implies that the effect is not entirely due to evaporation rate or alteration of the electrode interface but rather an effect on the crystallization kinetics during spin coating.

The relative degree of crystallinity was determined by x-ray diffraction spectroscopy. Crystalline P3HT gives rise to peaks at $2\theta = 5^\circ$ and 22° for the $\langle 100 \rangle$ and $\langle 010 \rangle$ planes, respectively.^{7,9,16} The more intense $\langle 100 \rangle$ diffraction signal was used for deducing the long-range order in the films.¹⁷ Figure 4 compares the diffraction signals for the control and the thiol-processed films, spun cast onto glass substrates, both before and after annealing. Based on a Gaussian fit for the normalized curves the relative peak widths at half maximum are 1.0, 1.12, 1.47, and 1.70 for BHJ-NA, BHJ-1%C8-NA, BHJ-1%C8-A, and BHJ-10%C8-A, respectively. The decreased width at half maximum and increased overall

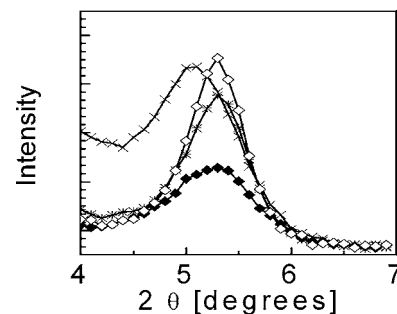


FIG. 4. X-ray diffraction results highlighting the $\langle 100 \rangle$ diffraction peak for P3HT in P3HT/PCBM films cast from toluene BHJ-NA (×), BHJ-A (*), BHJ-0.75%C8-NA (◆), and BHJ-0.75%C8-A (◇).

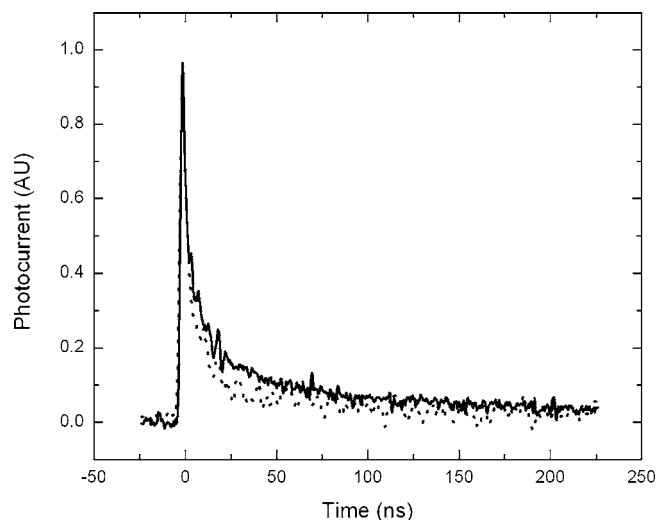


FIG. 5. Normalized transient photocurrent waveforms (at the peak) of films: BHI-NA (dotted line) and BHI-1%C8-NA (solid line).

intensity of the x-ray diffraction peak obtained from the thiol-processed samples indicates that the number and size of P3HT crystalline domains increase. The offset of the 2θ peak values in Fig. 4 corresponds to a different crystalline plane spacing, and may arise due to the residual solvent in the vicinity of the alkyl branches attached to the P3HT chains which expands the crystal structure parallel to the substrate.

Assuming that the number of carriers scales with optical absorption and given that the transmission spectra of the BHI-A samples are similar to the thiol-modified samples, it follows from Eq. (1) that processing with alky thiols modifies the product of carrier mobility and carrier lifetime. To determine changes in the carrier lifetime we performed fast ($t \geq 100$ ps) transient PC measurements. The transient PC wave forms, normalized at the peak photocurrent (in order to determine the change in the temporal profile), is illustrated in Fig. 5; the data indicate enhanced carrier lifetime in the samples processed using alky thiols. This increase in τ suggests an improvement in the ratio of shallow traps to deep traps that results from enhanced structural order. In contrast, with deep traps that greatly localize the carriers, shallow

traps enable higher mobility due to carrier hopping as well as excitation of the trapped carriers to the extended states, behavior that is consistent with significantly enhanced mobility.¹⁸

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