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Time-resolved terahertz spectroscopy of conjugated polymer/CdSe nanorod composites

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ABSTRACT

We report ultrafast carrier dynamics in hybrid CdSe nanorod / poly(3-hexythyophene) (P3HT) bulk heterojunction films measured by time-resolved terahertz spectroscopy, and compare to the well studied P3HT/phenyl-C61-butyric acid methyl ester (PCBM) blend. Both films show an improved peak photoconductivity compared to P3HT alone, consistent with efficient charge transfer. The photoconductivity dynamics show fast, picosecond trapping or recombination in the hybrid blend while the all-organic film shows no such loss of mobile charge over ns time scales. The ac conductivity for all samples is well described by a Kramers-Kronig compatible Jonscher-type power law with exponent between 0.5 and 1 suggesting that interchain hopping in the polymer or between nanorods occurs at frequencies higher than 3 THz immediately after photoexcitation.

Keywords: Terahertz, carrier dynamics, conjugated polymers, nanorods, bulk heterojunctions, conductivity, ultrafast

1. INTRODUCTION

The growing concern over renewable energy sources has lead to a search for new active materials for next generation photovoltaics (PVs) [1]. Organic semiconductors are an attractive candidate, due to the ease of processing from solution, their ability to be deposited on cheap and flexible plastic substrates and the potential to scale up deposition by cheap roll-to-roll processing [2] or inkjet printing [3]. However, these advantages have long been overshadowed by the relatively low power conversion efficiency of polymer PVs, limited to less than 6.1% in the best devices [4]. To a large extent this has been attributed to the low charge carrier mobility in conjugated polymers, particularly the electron mobility. This low mobility is due to the disordered nature of the polymer films, requiring carriers to hop among a disordered network to reach the electrodes. Moreover, the very nature of photoexcitations in polymer chains differs greatly from that of inorganic semiconductors. According to the Onsager picture [5], the primary photoexcitation is thought to be an exciton with a binding energy much larger than room temperature. Creation of charge carriers has required blending of the neat polymer with acceptor molecules such as fullerenes with a higher electron affinity, providing an interface where rapid charge transfer leads to an electron and hole or a polaron that are to some extent free to move with an applied field. The down side to this interpenetrating bi-continuous network of donor/acceptor media is an extreme sensitivity to the nanoscale morphology which dictates both the interfacial domain sizes facilitating charge creation, as well as the connectivity among those domains determining transport. A new class of materials, blending inorganic semiconductor nanostructures into a matrix of semiconducting polymer has shown promising results in recent years [6, 7]. In particular was the finding that increasing the aspect ratio of CdSe nanorods embedded in the poly(3-hexythyophene) (P3HT) lead to a marked increase in the external quantum efficiency, presumably because of the enhanced electron mobility as less hops are required among the CdSe nanorods to reach the electrodes [7]. It is therefore interesting to look at the ultrafast conductivity dynamics on a picosecond to nanosecond time scale to better understand this hopping process.

Time-resolved terahertz spectroscopy is a powerful probe of sub-picosecond conductivity dynamics in materials with the advantage of being a non-contact optical probe. The low energy of the THz pulse is below any interband transitions in

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Figure 1. A transmission electron microscopy image of the 20 nm long and 8 nm diameter CdSe nanorods.

either the polymer or isolated nanorods, and therefore it is intrinsically sensitive to mobile charge carriers. This technique has been used to examine charge carrier dynamics in organic semiconductors in solution [8], films [9, 10] and single crystals [11-13], as well as polymer bulk heterojunctions with organic acceptors [14-20]. Moreover, this technique has been used previously to identify signatures of excitons as well, where the non-resonant response of the polarizable exciton leads to a zero real conductivity and a negative and linear imaginary conductivity with frequency, equivalent to a purely real response for the electric susceptibility [19]. In this paper, we investigate the charge transport in both CdSe nanorods and P3HT/CdSe nanorod blends and benchmark their conductivity dynamics on a picosecond time scale against one of the most studied BHJ films, P3HT blended with the acceptor phenyl-C61-butyric acid methyl ester (PCBM). The transient complex conductivity for all BHJ films and a CdSe nanorod film can be described by a power law conductivity often applied to disordered systems in GHz frequencies and lower.

2. SAMPLE PREPARATION

Poly(3-hexylthiophene) was prepared according to the McCullough route [21] and was purified by Soxhlet extraction cycles employing in turn, methanol, acetone, hexane and finally chloroform. The product was precipitated from chloroform using methanol and finally dried in vacuum at 50 °C. The procedure was repeated twice giving a material with a regioregularity > 97% and $M_n = 18700$, $M_w = 36600$, $M_p = 33900$, PD = 1.9. [60]PCBM was prepared according to the literature [22] and purified by column chromatography. The film samples were prepared by dissolving P3HT and [60]PCBM in 1,2-dichlorobenzene at concentration of respectively 24 mg mL⁻¹ and 22 mg mL⁻¹ by stirring the solution for 24 hours at 90 °C under argon. The solution was filtered through a 0.45 micron filter immediately prior to drop casting onto the 0.5 mm thick c-cut sapphire substrate that had been ultrasonically cleaned for 15 minutes by submersion in subsequently water, isopropanol, acetone and chloroform.

CdSe nanorods approximately 20 nm long and 8 nm diameter, shown in the transmission electron microscopy image in Fig. 1, were prepared according to literature [23]. In a typical synthesis, 0.128 g (1 mmol) of CdO, 0.500 g (2 mmol) of DDPA and 3.0 g of TOPO were added into a three-neck flask equipped with a condenser and thermometer. The mixture was degassed for 15 min at room temperature and then refilled with nitrogen gas. Next, it was heated gradually to 330 °C and CdO was then dissolved in this mixture resulting in a colourless solution. The temperature was then reduced to 310 °C. A solution made of 0.078 g (1 mmol) Se and 2.0 g TOP was injected into the three-neck flask by multiple injections. The temperature was kept at 310 °C for another 30 min so that further growth can take place. The reaction was stopped by removing the flask from the heating mantle. The CdSe nanocrystals were dispersed in toluene and were then precipitated after centrifugation with the addition of methanol. The CdSe nanocrystals were redispersed in pyridine under reflux with heating at 65 °C for ligand exchange. TOPO (Tri-n-octylphosphine oxide, 99%) was purchased from Sigma Aldrich. CdO (Cadmium oxide, 99.95%) and TOP (Tri-n-octylphosphine, 90%) were purchased from Fluka. DDPA

Figure 2. A schematic of the time-resolved terahertz spectroscopy setup.

(Dodecylphosphonic acid, 100%) and selenium powder were obtained from Polycarbon, Inc. and Strem respectively. P3HT (poly-3-hexylthiophene) were purchased from Rieke Metals. P3HT:CdSe film samples were prepared in a binary solvent consists of 10 v/v pyridine in chloroform. The weight ratio of P3HT:CdSe was 1:9. The solution was then drop casted onto the substrate.

3. METHODOLOGY

Optical pump-THz probe experiments were performed using a femtosecond laser amplifier providing 3.5 mJ, 35 fs duration pulses centered at 800 nm at a 1 kHz repetition rate. A schematic of the experimental setup is shown in Fig. 2. The output of the laser system is split into a pump and another beam that is delayed by a mechanical delay stage (D1) before it is split into a THz generation beam and an optical gating beam for THz detection. The generation beam passes through another delay line (D2) before it is incident on a 1.4 mm thick [010] cut N-benzyl-2-methyl-4-nitroaniline (BNA) crystal, generating a THz pulse by optical rectification. BNA has an extraordinarily high second order nonlinearity with a linear power dependence of the THz electric field up to its damage threshold at 1 mJ/cm², also producing both a high bandwidth and dynamic range. The 5 mm diameter of the generation beam produces a nearly collimated THz pulse that is beam expanded by a factor of 4 by two off-axis parabolic mirrors to a diameter of 20 mm. This large THz beam is then focused to approximately 1 mm diameter spot at the sample position, is recollimated upon transmission and is then focused onto a 0.5 mm thick ZnTe or 0.3 mm thick GaP crystal for detection. The pump beam is frequency doubled in a 1 mm thick β -BBO crystal with a 400 nm Schott glass filter, and focused through a small hole in the back of the parabolic mirror before the sample position enabling co-linear excitation with the THz probe beam. The diameter of the pump beam is 2.2 mm FWHM at the sample position, ensuring homogeneous excitation of the sample mounted on the back of a 1.5 mm diameter aperture that both aids in alignment of the pump and THz beams and guarantees that only photoexcited portions of the film are probed by THz transmission. A custom chopper wheel modulates the pump and THz generation beams at the second (500 Hz) and third (333 Hz) harmonic of the laser repetition rate, respectively. These modulations are used as triggers for two separate lock-in amplifiers. As outlined previously, this enables simultaneous detection of both reference and differential scans, eliminating any influence of long term drift in the laser power, alignment or timing [24].

There are two modes of operation for TRTS, a differential transmission ($-\Delta T/T_0$) scan and a full frequency resolved scan that allows extraction of the complex conductivity over the bandwidth of the THz pulse. In a differential scan, a single

Figure 3. Differential THz transmission $-\Delta T/T_0$ for (a) P3HT and (b) P3HT:PCBM films after 400 nm excitation at a fluence of 1.9 mJ/cm^2 .

point in the THz electric field is monitored as a function of pump-probe delay time, yielding information on the dynamics of the excitation and subsequent relaxation in the material. In a full scan, the entire THz waveform is recorded at a specific pump-probe time delay, which yields the electrodynamics of the material at that instant in time in the form of the complex conductivity or dielectric function, equivalently. In all cases the films were thick enough to completely absorb the pump light. Double modulation yields simultaneously detected waveforms, E_1 and E_2 , from the modulation of the THz generation beam and the pump beam, respectively. These in turn can be related to the THz transients in the absence, E_{ref} , and in the presence, E_{pump} , of an excitation. Fourier transformation of these waveforms yields the complex transmission function, $T = E_{\text{pump}}(\omega)/E_{\text{ref}}(\omega)$ which can in turn be related to the complex sheet conductance $\sigma_s = \sigma_1 + i\sigma_2$ of the photoexcited film by [25]

$$\tilde{T}(\omega, \Delta t) = \frac{E_{\text{pump}}(\omega, \Delta t)}{E_{\text{ref}}(\omega, \Delta t)} = \frac{N + 1}{N + 1 + Z_0 \tilde{\sigma}_s(\omega, \Delta t)} \quad (1)$$

where N is the index of refraction of the sapphire substrate at THz frequencies (3.07) and Z_0 is the impedance of free space (377 Ω).

Figure 3(a) shows the differential THz transmission for the drop cast P3HT film on sapphire, after 400 nm excitation with a pump fluence of 1.9 mJ/cm^2 , and THz delay set to correspond to a maximum differential signal $-\Delta E_{\text{max}}$. The risetime is limited by the resolution of the setup, approximately 0.5 ps, and the decay is well described by a power law of the form $-\Delta T/T_0 = At^\beta$ with $\beta = 0.338 \pm 0.004$. The power law form is a typical signature of dispersive transport, a common form for photoconductivity in models of hopping conduction with multiple trapping [26]. A power law decay has previously been predicted for the photoconductive decay of P3HT in the absence of impurities [27], and observed in a wide variety of single crystal organic semiconductors [9, 11]. The addition of the methanofullerene acceptor PCBM to the film, shown in Fig. 3(b), leads a doubling of the peak photoconductivity. This is in agreement with other TRTS studies on P3HT:PCBM films [15, 17], but in disagreement with others where they saw a decrease [14]. A dramatic increase in photoconductive lifetime is observed with a long-lived ($> 1 \text{ ns}$) component appearing, in agreement with previous work [14, 15, 19]. The form of conductivity can be well described by a combination of a power law decay with an exponent of -0.33 and an exponential decay with a lifetime beyond that resolved by the length of the scan. Previous traditional photoconductive measurements have shown the free carrier lifetime to be as high as 1.5 ns [28].

The differential transmission for the CdSe nanorod and P3HT:CdSe nanorod BHJ film are shown in Fig. 4 for the same excitation conditions as the all-organic films discussed above. The initial peak photoconductive response is approximately 30% greater for the hybrid BHJ film than for the all-organic P3HT:PCBM film, for the same excitation. We note that differences in optical absorption of each film cannot directly account for this difference as the entire pump

Figure 4. Differential THz transmission, $-\Delta T/T_0$, for CdSe nanorods (solid circles) and P3HT:CdSe nanorod composites (open circles) following 400 nm excitation at a fluence of 1.9 mJ/cm^2 . The lines are fits to a power law decay of the form $-\Delta T(t)/T_0 = At^{-\beta}$ with exponents given in the text.

fluence is absorbed by both films and it is the sheet conductivity that is measured by THz transmission. The photoconductive decay for both the CdSe nanorod film and hybrid BHJ film can be well described by a power law, with $\beta = 0.537 \pm 0.005$ and $\beta = 0.524 \pm 0.002$, respectively. This similarity between the dynamics of these two films indicates the hybrid BHJ film conductivity is dominated by charges on the CdSe nanorod network. The dispersive nature of nanorod, hybrid and P3HT films suggests that the photoconductive dynamics are a property of the disordered lattice of transport sites.

The complex conductivity spectrum for the four samples is shown in Fig. 5, taken 1 ps after photoexcitation. The similarity in the shape of each spectrum is remarkable. These features are similar to that observed in many disordered semiconductor systems previously investigated by TRTS, namely that the real conductivity increases with frequency, the imaginary conductivity is negative and both real and imaginary components are comparable in magnitude over the THz bandwidth [17, 19, 20, 25, 29-33]. This is in contrast to what is expected from a band semiconductor, normally well described by the simple Drude form. The increasing σ_1 with frequency has long been observed in disordered materials and indeed one should not be surprised to see such behaviour in any material that is made of different conducting phases or may be characterized by hopping transport. The physical picture for composite materials is as the frequency increases the contribution from smaller regions in the sample to the ac conductivity is greater. The negative imaginary conductivity can also be physically understood from having conducting regions separated by a less conducting phase, which describes a capacitor and thus σ_2 has a negative low frequency capacitive response rather than the positive inductive response given by free charge carriers.

The conductivity of the P3HT film shown in Fig. 5(a) cannot be described by an excitonic response alone. The largest possible excitonic conductivity is shown as a dotted line, estimated by the Clausius-Mossotti relation with an exciton polarizability of $20 \text{ \AA}^3$ [18] and a maximum exciton sheet density of $3.9 \times 10^{19} \text{ m}^{-2}$ assuming 100% conversion of photons to excitons and relating the conductivity to the permittivity by $\sigma_2 = -i\omega\epsilon_0\epsilon$. In addition, there is a measurable non-zero real conductivity that indicates the presence of mobile charge carriers on these ultrafast time scales, in agreement with previous TRTS work on the charge generation efficiency in P3HT films [18]. The addition of an electron acceptor PCBM to P3HT increases σ_1 in the BHJ P3HT:PCBM film shown in Fig. 5(b), and can be attributed to more charge carriers being created as a result of exciton dissociation at P3HT:PCBM domain interfaces.

The ac conductivity of hopping transport in disordered condensed matter systems is often well described by a ‘‘Jonscher power law’’ $\sigma_1(\omega) = \sigma_{dc} + \omega^\alpha$ with $\alpha \leq 1$ [34]. The frequency range where this applies is often quoted to be below GHz frequencies or below the maximum hopping rate. However, it was recently found that this law also applies to a wide range of disordered condensed matter systems beyond GHz frequencies into the THz regime [35, 36]. Here we show the

Figure 5. Complex sheet conductivity 1 ps after photoexcitation with 400 nm light at a fluence of 1.9 mJ/cm² for (a) P3HT, (b) P3HT:PCBM, (c) CdSe nanorods and (d) P3HT:CdSe nanorods. Lines are fits to the model described in the text.

complex conductivity of polymers, nanorod films and blends of the two are also described quite well by this power law behavior. This common THz conductivity response among three different samples is a good indication that no specific microscopic feature of the samples is responsible for the spectral shape, but rather it is completely described by a universal curve valid for disordered systems where hopping transport between localized states is likely to occur.

A power law ac conductivity response can be put into a Kramers-Kronig compatible form $\sigma(\omega) = A(-i\omega)^\alpha$ where the real and imaginary components are given as

$$\sigma_1(\omega) = A\omega^\alpha \cos(\alpha\pi/2) \quad (2)$$

$$\sigma_2(\omega) = -A\omega^\alpha \sin(\alpha\pi/2) \quad (3)$$

This form accounts for the similarity in the shapes of both real and imaginary components, as they both follow the same power law and only differ in magnitude depending on the value of the exponent. Fig. 5 shows the results of simultaneous numerical fits using Eq.'s (2) and (3) to the complex conductivity data for P3HT, P3HT:PCBM, CdSe nanorods and P3HT:CdSe nanorods. All four samples are very well described by this functional form over the bandwidth of the THz pulse. The extracted scaling parameter A and exponent α from these fits are shown in Table 1. During these fits, a dc conductivity was added to the real component and allowed to vary, although it was always suppressed to zero. The magnitude of the conductivity response increases as the exponent α decreases from 0.87 for the P3HT film to 0.50 for the P3HT:CdSe nanorod blend. This is to be expected from the unit analysis of A . A second method of extracting the exponent for a conductivity that follows Eq.'s (2) and (3) other than numerical fitting is through the relation $\alpha = 2/\pi \text{atan}(|\sigma_2|/\sigma_1)$. Indeed the ratio $|\sigma_2|/\sigma_1$ is found to be constant over the THz pulse bandwidth, yielding values of α given in Table 1 that are found to agree very well with the numerical fits.

Table 1. Fit parameters for the Kramers-Kronig compatible power law given by Eqs. 2 and 3 applied to the data in Fig. 5.

Sample	A ($\mu\text{S s}^{-\alpha}/\text{sq}$)	α (fit)	$\alpha=2/\pi \text{atan}(\sigma_2 /\sigma_1)$
P3HT	37 ± 1	0.89 ± 0.02	0.87 ± 0.03
P3HT:PCBM	96 ± 2	0.69 ± 0.01	0.69 ± 0.01
CdSe nanorods	213 ± 4	0.56 ± 0.01	0.57 ± 0.02
P3HT:CdSe nanorods	278 ± 4	0.51 ± 0.01	0.50 ± 0.02

4. CONCLUSIONS

In summary, we have examined the photoconductivity dynamics of hybrid CdSe nanorod/P3HT bulk heterojunction films and compared them to both the neat P3HT, a CdSe nanorod only film and the most commonly used blend of P3HT:PCBM. The peak photoconductivity is highest for the hybrid BHJ film, however this quickly undergoes power law decay while the P3HT:PCBM film retains a significant level of conductivity for over a ns. The nanorod, hybrid BHJ and neat P3HT films all demonstrate dispersive transport in the form of power law decays, which we attribute to hopping on a disordered lattice. The frequency resolved complex conductivity spectrum taken 1 ps after excitation is also consistent with a model of carriers hopping on a disordered lattice, being in good agreement with a Kramers-Kronig compatible “Jonscher law” for disordered conductors despite this traditionally being only valid for frequencies below the GHz regime.

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