

Surface plasmon enhanced absorption dynamics of regioregular poly(3-hexylthiophene)

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An increased absorption of regioregular poly(3-hexylthiophene) due to surface plasmons (SPs) has been studied by steady state fluorescence spectra measurements and femtosecond transient absorption (TA) technique. The SPs were excited by periodic Ag grating structures transferred from the photoresist gratings which were fabricated by two-beam laser interference. The steady state fluorescence measurements show a maximum enhanced fluorescence of about 16 times larger arising from the absorption enhancement. Further investigation by TA technique reveals that the yield of the polaron pairs on Ag gratings significantly increase, much bigger than that of the pure sample, which also confirms the enhanced absorption efficiency as resulting from the excited SPs. © 2011 American Institute of Physics. [doi:10.1063/1.3590728]

Recently, the interest in thin-film polymer solar cells has significantly grown because of their low cost, easy fabrication, light weight, and flexibility. The power conversion efficiency of polymer solar cells has reached 7% for blends of low band gap polymers.^{1,2} However, further enhancement of the efficiency is still required for practical applications. In bulk-heterojunction solar cells, the generation of photocurrent is a cascade of four steps: generation of excitons by photon absorption, diffusion of excitons to the donor-acceptor interface, dissociation of the excitons into free charge carriers, and transport of these carriers to the electrodes. Among these steps, the efficiency of light absorption and charge carrier transport are the two most important areas in efficiency improvement.³ So one of an effective approach to enhance the power conversion efficiency is to increase the light absorption efficiency of the polymer layer. However, because of the poor charge carrier mobility of typical polymers, the film of absorbing layer should be thin enough for photogenerated carriers to reach the electrodes before recombination. To overcome this deficiency, efficient light trapping techniques such as folded device architectures,^{4,5} photonic crystal,⁶ surface plasmon resonance,⁷⁻¹¹ and diffraction gratings^{12,13} have been investigated. Among these, using periodic metal gratings to trigger SPs has demonstrated promising prospect, which enhances the local electromagnetic field at the metal/polymer interface and efficiently couple the light into the active layer to improve the absorption efficiency of the photoactive layer.^{14,15} Regioregular poly(3-hexylthiophene) (RR-P3HT) is one of the most efficient organic photovoltaic materials and have been investigated intensively as a model material for solar cells. In this letter, we introduce Ag grating nanostructures to P3HT thin film and study how efficient could the grating enhance the light absorption for this typical polymer. Both steady state fluorescence measurements and femtosecond transient absorption (TA) measurements were performed to the films with

and without Ag gratings. A dramatical increasing of the photoactive layer absorption for films with gratings was demonstrated.

The sample structures are illustrated in the inset of Fig. 1, comprising glass/photoresist/Ag/P3HT. Regioregular P3HT with Mw=60k and regioregularity greater than 95% were purchased from Luminescence Technology Corp. and used without further purification. The samples were fabricated as following. First, the photoresist was deposited onto the precleaned glass substrates by spin-coating, and the grating structures were produced by two-beam laser interference on the photoresist.^{16,17} 50 nm thick Ag was deposited on the photoresist gratings and the active layer for P3HT was spin-coated from solution of RR-P3HT dissolved in chloroform at a concentration of 5 mg/mL. Through this process, a grating structure was transferred from the photoresist layer to Ag and P3HT layers. The films were annealed at 150 °C for 30 min before sealed with another glass slide. To avoid degradation by oxygen, the spin-coating and sealing process were done under nitrogen environment in a glove box with an oxygen concentration smaller than 0.1 ppm. Three samples were prepared, two with grating periods of 320 nm and 350 nm,

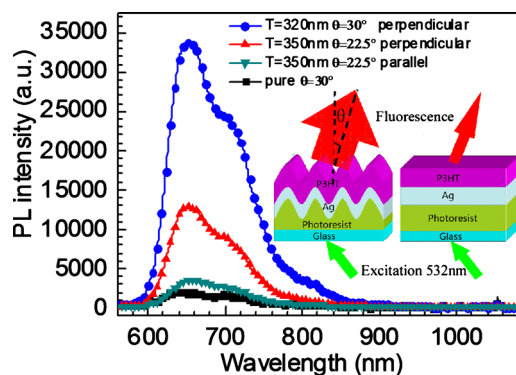


FIG. 1. (Color online) Steady state fluorescence spectra of the three samples. The inset gives schematic of the fabricated samples with the structure of glass, photoresist, Ag and P3HT from bottom to top.

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respectively, and a reference one without grating.

Steady state fluorescence of the three samples were measured in transmittance mode, excited with 532 nm light from a laser diode and the excited light polarization was perpendicular to the grating pitch direction. Because the fluorescence intensity from the polymer on metal gratings relies on SPs are highly sensitive to the angle,¹⁸ fluorescence spectra were recorded at varying angles of θ with an AvaSpec-2048 fiber optic spectrometer at 0.6 nm resolution. As shown in Fig. 1, the fluorescence intensity of the samples with grating structures were much higher than that of the pure sample without grating structures. Especially, the sample with the grating period of 320 nm, the maximum fluorescence intensity at the emission angle of $\theta=30^\circ$ was approximately 16 times larger than that of the pure sample. Generally, there are two main reasons for the enhanced fluorescence, namely, absorption enhancement and SP coupled emission. The absorption enhancement can only influence the fluorescence intensity and do not affect on the spectrum shape while in the case of SP coupled emission, both the fluorescence intensity and the spectrum shape will be changed.¹⁹ Therefore, we can get the conclusion that the enhanced fluorescence should be due to the increased absorption caused by the excited SPs which could enhance the near-field electromagnetic and efficiently couple the light into the P3HT layer. Since the SPs can only be induced by the incident light with polarization perpendicular to the grating pitch direction.¹⁹ In order to demonstrate the absorption enhancement is really arising from the SPs, we further excited the 350 nm periodic sample with the incident light polarization parallel to the grating pitch direction. The fluorescence enhancement was much smaller than that excited with the light polarization perpendicular to the grating pitch direction (Fig. 1), which confirms the absorption enhancement is related to the SPs.

To further verify the absorption enhancement mechanism, femtosecond TA experiments were performed in these samples. As is well known in P3HT film,²⁰ the polaron pairs are generated from a higher singlet excitation state due to nonradiative exciton–exciton (E–E) annihilation, which has more yield at higher exciting densities. So, the absorption enhancement can be demonstrated by comparing of the polaron pairs formation yield in different samples.

The TA setup used in this work has been described in detail elsewhere.²¹ We used a reflection mode TA system, where the angle between the probe beam and the normal of the sample was 37° and Ag film was used as a mirror to facilitate reflection mode TA measurements. The excitation wavelength was set at 620 nm. Figure 2 shows the TA spectra of the three samples at 20 nJ/pulse. The negative signal (from 500 to 620 nm) result from the ground state bleaching while the positive signal around 650 nm is mainly due to the polaron pair absorption.²⁰ As one can see that the amplitude of polaron pair absorption is much stronger for samples with metal gratings than that of the pure sample. It means that much more polaron pairs are generated via E–E annihilation on samples with Ag gratings, which must be due to the enhanced density of the singlet excitons. It indicates that, owing to the introduced periodic Ag gratings, the total absorbed light by the P3HT layer is enhanced, resulting more generation of the singlet excitons. The enhancement of the E–E annihilation can be also revealed by the bleaching recovery dynamics (Fig. 3). At the early stage, the bleaching recovery has a short time constant due to the singlet E–E annihilation.

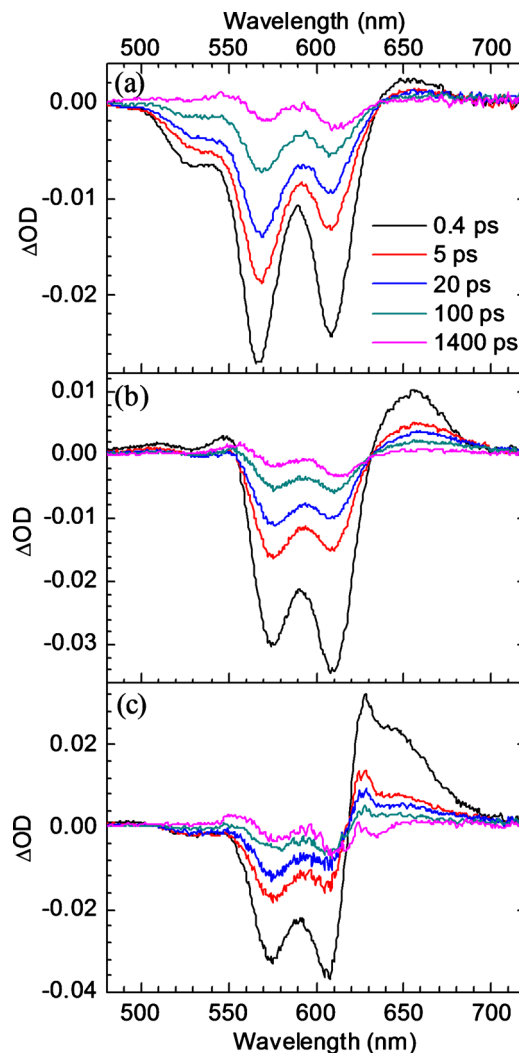


FIG. 2. (Color online) TA spectra recorded at 0.4 ps, 5 ps, 20 ps, 100 ps, and 1400 ps, respectively, of P3HT on (a) pure Ag film, (b) Ag gratings with period of 350 nm, and (c) Ag gratings with period of 320 nm. The excitation wavelength is 620 nm and the excitation pulse intensity is 20 nJ/pulse.

The normalized bleaching recovery of P3HT on Ag gratings decayed faster than that of the pure sample, indicating that the E–E annihilation processes were increased due to the enhanced absorption of the P3HT.

Finally, to quantify the efficiency of the enhanced absorption due to metal gratings, intensity dependent TA experiments of the three samples were carried out. According to the previous reports,²⁰ the lifetime of the polaron pair is

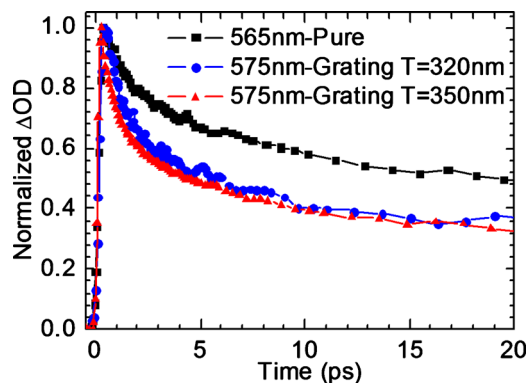


FIG. 3. (Color online) TA dynamics at one peak of the photobleaching spectra at excitation intensity of 20 nJ/pulse.

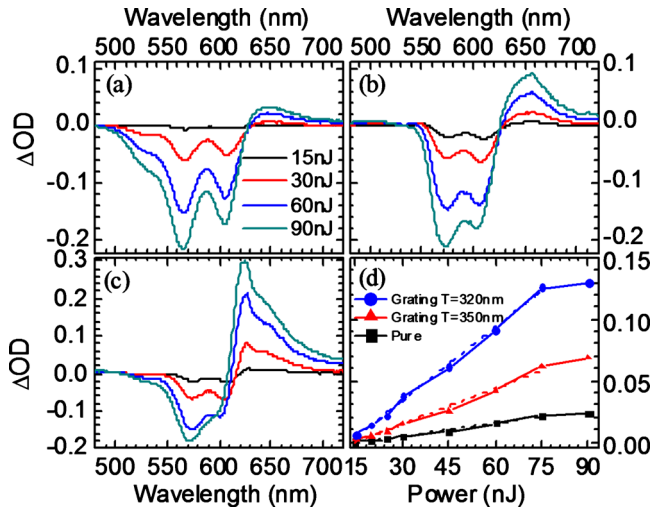


FIG. 4. (Color online) Differential transient spectra of 4 and 0.4 ps, which is mainly from polaron pair of P3HT on (a) pure Ag film, (b) Ag gratings with period of 350 nm, and (c) Ag gratings with period of 320 nm. (d) Differential transient signals of 4 and 0.4 ps of P3HT films of the three samples at 650 nm (polaron pair) against the excitation intensity.

0.7 ps and almost decay out at 4 ps, so we subtract the spectra of 4 ps from the spectra of 0.4 ps, where the spectra grow to maximum. The different spectrum roughly reflects spectral shape only caused by the polaron pairs decay [Figs. 4(a)–4(c)]. As mentioned above, the yield of polaron pairs is strongly dependent on the pump power, which increases with the increasing excitation intensities. The excitation intensity dependent polaron pair yields of the three samples are shown in Fig. 4(d). Comparison of the three curves reveals that much more of the polaron pairs were generated from the P3HT on Ag gratings at same excitation intensities, especially with the grating period of 320 nm. In addition, all three transient signals exhibited a linear power dependence below excitation intensity of 75 nJ/pulse with the slopes of 1.99×10^{-3} , 9.7×10^{-4} , and 3.62×10^{-4} for 320 nm, 350 nm grating, and pure P3HT film, respectively. The slope of the pure sample is much smaller than that with metal gratings. With the increasing excitation intensities, the yield of the polaron pairs on Ag gratings increased more significantly. These results further support that the absorption efficiency of the polymer layer was enhanced due to the introduced metal gratings.

Moreover, we notice that the absorption enhancement is more efficient by the grating with period of 320 nm, which can be attributed to the good match between the SPs absorption region and the excitation wavelength 620 nm. Because it is difficult to directly measure the SPs absorption spectra of the gratings with P3HT layer, the SPs absorption of the pure Ag gratings were measured. Without P3HT layer the SPs absorption peak of the grating with period of 350 nm matches well with the excitation wavelength. While the position of SPs absorption peak is highly sensitive to the refractive index of local dielectric environment on the metal gratings, which was found to have a redshift with the increased refractive index.²² We have done numerical simulations with scattering matrix theory to simulate the SPs absorption spectra for grating samples with and without the P3HT layer and the results show that the SPs absorption peak shows a redshift by tens of nanometer after coated with P3HT layer. After such a large redshift, the SPs absorption peak of the 320 nm peri-

odic Ag gratings with P3HT will match better with the excitation wavelength of 620 nm than the 350 nm periodic Ag gratings with P3HT and lead to a stronger absorption enhancement for 320 nm gratings.

In conclusion, both the steady state fluorescence and TA measurements show that the introduced periodic Ag grating structures substantially enhanced the absorption efficiency of the P3HT layer. The steady state fluorescence measurements show a maximum enhanced fluorescence about 16 times larger for the P3HT coupled to the Ag gratings with period of 320 nm. The TA experiments reveal that periodic Ag gratings can significantly enhance the generation of polaron pairs, and the polaron pair yields increased more obviously with increasing excitation intensities. The increasing yield of polaron pairs also confirms the enhanced absorption due to gratings. These demonstrate that Ag grating plays a crucial role in enhancing the absorption efficiency of the active polymers. Due to enhanced near-field coupling, the total absorbed photons by the photoactive layer in polymer solar cells containing metal gratings is significantly enhanced, which can effectively resolve the conflicts between light absorption and the poor charge carrier mobility of the polymer.

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