Plasmon–Polaron Coupling in Conjugated Polymer on Infrared Nanoantennas

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Supporting Information

ABSTRACT: We propose and demonstrate a novel type of coupling between polarons in a conjugated polymer and localized surface plasmons in infrared (IR) nanoantennas. The near-field interaction between plasmons and polarons is revealed by polarized photoinduced absorption measurements, probing mid-IR polaron transitions, and infrared-active vibrational modes of the polymer, which directly gauge the density of photogenerated charge carriers. This work proves the possibility of tuning the polaronic properties of organic semiconductors with plasmonic nanostructures.

KEYWORDS: Localized surface plasmons, IR nanoantennas, conjugated polymer, polarons

The coupling of plasmons to various degrees of freedom, such as molecular vibrations,1,2 phonons,3,4 and excitons5−7 in hybrid nanostructured materials is a subject of intense investigation. Local electric field enhancement in the vicinity of plasmonic nanostructures is regarded as an effective light-trapping technique8,9 and also as a method to modify the photophysical properties of materials.10,11 In the area of organic semiconductors, applications of plasmonic nanostructures range from the enhancement of light emission and collection efficiency in light-emitting devices12 to the improvement of light harvesting in thin-film photovoltaics.13,14 Specifically, coupling of triplet states in polymers with near-IR plasmon resonances of silica core−gold shell nanoparticles allowed inducing quenching of radiative triplet exciton recombination and reducing polymer susceptibility to photo-oxidative degradation.6 In thin film polymer photovoltaics, plasmonic electric-field enhancement is often used to increase light absorption by coupling surface plasmon resonances with excitonic transitions of the polymer, at energies above the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) gap.15 Increased probability of exciton dissociation via plasmon−exciton coupling has also been reported.16−18 While neutral exciton species are responsible for light absorption and emission properties of organic materials, self-localized polarons induced by strong electron−phonon coupling fully determine their charge transport characteristics.19,20 Unlike previous studies on plasmon hybridization with excitons in organic semiconductors, here we focus on the interaction between surface plasmons and photogenerated polarons in a conjugated polymer. By engineering a plasmonic metamaterial resonant with characteristic infrared polaronic transitions, we provide evidence, for the first time, of plasmon−polaron coupling as a means to modify charged photoexcitations of organic materials.

The proposed concept is illustrated in Figure 1a. Photogenerated polarons along the polymer backbones interact with localized surface plasmons in the adjacent IR nanoantennas, which resonate at characteristic mid-IR polaron energies far from excitonic absorption. Plasmon−polaron coupling is

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expected to resonantly enhance oscillator strength of polaronic transitions and to possibly alter the polaron relaxation and exciton dissociation dynamics. To test this concept we chose the well-characterized organic photovoltaic material regioregular poly(3-hexylthiophene) (rr-P3HT) whose chemical structure is shown in Figure 1b. P3HT is a low-bandgap polymer (HOMO−LUMO gap ~1.9 eV) with absorption spectrum (solid black curve in Figure 1b) well overlapped with solar irradiance. As first suggested by the Su−Schrieffer−Heeger (SSH) tight-binding model, the generation of polarons in conjugated polymers results in the formation of new intragap states associated with positive and negative polaron relaxation energies (Figure 2a). In P3HT, such intragap states lead to the appearance of two infrared optical transitions (P1 and P2 in the left diagram in Figure 2a); the corresponding photoinduced absorption (PIA) spectrum in Figure 2b shows P1 and P2 polaron absorption bands around 0.33 and 1.24 eV, respectively. In addition to polaron transitions, characteristic infrared active vibrational (IRAV) modes due to the presence of charged species on the polymer chain are evident at the low-energy side of the PIA spectrum, below 0.16 eV. The intensity of polaron transitions and IRAV modes can be used as a unique gauge for charge carrier density in conjugated polymers.

To induce coupling between plasmon and polarons, we designed and fabricated metal nanostructures with resonant features overlapped with the P1 polaron band and negligible absorption in the visible part of the spectrum to avoid plasmonic enhancement of excitonic absorption. For similar reasons, we avoided coupling with P2 because of its overlap with the broadband excited state absorption of interchain excitons (EX) at 1.05 eV. The structure of choice was a split-ring resonator (SRR) with geometrical parameters shown in Figure 2c. The corresponding transmission spectra obtained by numerical simulations for orthogonal polarizations of the incident light are shown in Figure 2d (polarization directions with respect to SRR gap orientation are depicted as a blue arrow for 90° and a red arrow for 0° in Figure 2c). A single
resonance around 0.37 eV (A in Figure 2d) is excited in the region of interest for 90° polarization, while two resonances appear in the same region, at 0.19 eV (B) and 0.53 eV (C) for 0° polarization of the incident wave. The energy diagrams of these three transitions are shown alongside the P3HT plasmonic transitions in Figure 2a; when taking into account the red-shift induced on plasmonic resonance frequency by the high-index polymer film, the A and B plasmonic resonances are optimally aligned with the P1 transition and the IRAV modes of P3HT. Normalized field distributions of the electric field component perpendicular to the plane of the structure (\(E_z\)) 20 nm above the substrate plane for each SRR resonance are plotted in Figure 2c and show near-field confinement of the fields due to surface plasmon resonant modes in the SRR. Clear dipolar modes can be identified for A and B, while a quadrupolar mode is excited at higher frequency (C) as expected.

On the basis of this design, large-area SRR samples were fabricated using hole-mask colloidal nanolithography with tilted-angle-rotation evaporation, a proven technique for low-cost and large-area fabrication of complex plasmonic nanostructures and metamaterials (see Supporting Information for sample fabrication methods). Resulting samples comprise a dense array of SSRs, where the metamolecules are randomly distributed but share a common rotational orientation throughout the entire substrate (see electron microscopy image in Figure 2e). Consequently, large-area transmission spectra of fabricated structures for 0° and 90° light polarization (Figure 2f) agree very well with simulations obtained with periodic boundary conditions (Figure 2d). Following the design requirements, the fabricated IR-nanoantennas have very low absorbance (OD < 0.1) in the visible part of the spectrum overlapped with absorption of P3HT (red dashed curve in Figure 1b). Absence of plasmonic enhancement of polymer absorption is confirmed by the slight quenching of P3HT film absorption (black solid curve in Figure 1b) on the IR-nanoantennas (red solid curve in Figure 1b). This ensures that visible excitation (e.g., at 532 nm, green arrow in Figure 1b) of the hybrid metamaterial/polymer sample photoexcites the polymer but not the IR-nanoantennas. The topography of the IR-nanoantennas/P3HT sample shows a homogeneous coverage of polymer film with thickness of 70 nm (Figures S1 and S2 in Supporting Information).

Polarized infrared transmission of the hybrid film is shown in Figure 3a. Both spectra obtained with 0° and 90° polarizations (red and blue curves) present characteristic features of P3HT (e.g., the hexyl C−H stretching vibrational modes at ~0.36 eV) as well as of the nanoantennas (e.g., polarized resonances). The high refractive index (n ~ 1.85) of the polymer film induces a red shift of about 0.06 eV of the nanoantenna resonances with respect to the bare antennas (Figure 2f). Moreover, interaction between the surface plasmons of the SRR and the polarons in the polymer occurs in the near-field of the nanostructures, whereby near-field resonances are typically red shifted when compared to the far-field response. This near-field shift is well described by a damped harmonic oscillator model driven by an external light field. Figure 3b shows the simulated near-field spectra of our SRRs corresponding to the fitting parameters of Lorentz oscillators extracted from the transmission spectra in Figure 3a, where near-field resonances are further red shifted by ~0.11 eV compared to the far field ones.

To probe the interaction between resonant surface plasmons and polarons in the hybrid metamaterial/P3HT system we
conducted broadband steady-state PIA experiments at low temperature, $T = 78$ K, using visible laser excitation as the “pump” and the polarized broadband beam of a Fourier-transform infrared spectrometer as the “probe”; the corresponding differential transmittance spectra are reported in Figure 3c (see measurement descriptions in Supporting Information). The PIA of the hybrid metamaterial/P3HT sample is found to be independent of pump beam polarization but strongly dependent on the polarization of the probe. As anticipated, the resonant enhancement of PIA spectra coincides with the near-field resonances calculated in Figure 3b, which can be regarded as strong evidence of plasmon–polaron coupling. Moreover, for both 0° (red solid curve) and 90° (blue solid curve) polarizations the amplitude of PIA resonances is enhanced by a factor of approximately two compared to the reference pristine P3HT film (black solid curve), indicative of plasmon-induced enhancement of the polaron density. The actual enhancement factor of the PIA signal is masked by the strong modulation features appearing at 0.14 and 0.41 eV for the 0° polarization and at 0.29 eV for the 90° polarization, which make a quantitative analysis difficult. To further understand these modulation features, we subtracted the PIA signal of IR-nanoantennas/P3HT from that of pristine P3HT. The resulting spectrum shows photobleaching of P3HT polaron absorption induced by the IR-nanoantennas, which may be attributed to the resonant transfer of charges into corresponding P3HT polaron states upon the excitation of IR-nanoantennas (Figure S3 and discussions in Supporting Information). To rule out other factors such as charge or energy transfer from the polymer to the nanoantennas, we fabricated a control sample with plasmonic nanoantennas off-resonance with respect to polarons mid-infrared (MIR) transitions (Figure 3d) and characterized it under the same experimental conditions (the characterization of the off-resonance sample is shown in Figure S4 in Supporting Information). In this case, probe-polarized PIA spectra of the control sample show very similar behavior to that of pristine P3HT films with no significant enhancement of the polaron signal (Figure 3e).

The effect of plasmon–polaron coupling is also reflected by changes of vibrational absorption spectra of P3HT upon photodoping. Various theoretical studies describe the appearance of strong IRAV modes when even parity symmetric Raman-active vibrational modes ($A_g$ modes) are converted into IR-active modes by the local symmetry breaking of polymer chains produced by charge localization. Experimental infrared absorption spectra induced by photo- or chemical-doping show peaks with one-to-one correspondence to the strongest Raman-active modes of the polymer observed in resonance Raman scattering. The intensity of these IRAV modes is directly proportional to charge carrier concentration, making them a unique optical probe for charge carrier density and dynamics in conjugated polymers. Instead of manifesting as PIA peaks, IRAV modes of P3HT films possess a Fano-type antiresonance line shape (Figure 4b), created by the superposition of the narrow IRAV modes with the broadband delocalized polaron absorption. In Figure 4b, we compare the IRAV modes of the pristine polymer film (black curve) with those obtained from the hybrid P3HT sample with orthogonal probe polarizations. For 90° polarization (blue curve), the IRAV modes appear in a spectral region not strongly modulated by the plasmon–polaron coupling resonance at $\sim 0.3$ eV; nevertheless, their intensity is enhanced by more than a factor of 2 and all modes are preserved without spectral shift with respect to the pristine film. In both pristine and hybrid samples at 90° probe polarization (black and blue curves in Figure 4b), the assignment of IRAV modes to P3HT IR-absorption (Figure 4a) and resonance Raman (Figure 4c) modes is hindered by the presence of antiresonances (indicated by gray arrows). In contrast, at 0° probe polarization the IRAV modes overlap with the plasmon–polaron coupling resonance at $\sim 0.15$ eV, and their peaks are easily resolved (red curve in Figure 4b): from 900 to 1300 cm$^{-1}$, the antiresonances become positive IRAV peaks perfectly matching the Raman active modes, whereas in the tail of the modulation from 1300 to 1700 cm$^{-1}$ the IRAV peaks become antiresonances, also in correspondence with Raman active modes. We therefore speculate that the near-field coupling of plasmons and polarons offsets the effect of broadband delocalized polaron absorption in the spectra, thus making IRAV modes of P3HT clearly distinguishable; these experimental results are consistent with the description from nonadiabatic amplitude mode theory developed by Horovitz and colleagues. The enhancement of IRAV modes in both 0° and 90° polarized PIA spectra may suggest that more charges are generated in IR-nanoantennas/P3HT hybrid sample. To further elucidate the plasmon–polaron coupling mechanism and its effect on inherent photophysical properties of the polymer, such as polaron generation, we compare infrared PIA spectra to differential transmittance spectra obtained upon chemical (redox) doping of pristine P3HT and P3HT on resonant nanoantennas (Figure S5). By chemically introducing charge carriers, we rule out the possibility that the enhancement observed in PIA spectra may arise from additive effects of plasmonic and polaronic absorption resonances and
Figure 5. Chemical doping-induced absorption spectra of P3HT on nanoantennas. (a) Transmission spectra of undoped IR-nanoantennas/P3HT hybrid sample with 0° (red curve) and 90° (blue curve) light polarizations. (b) Chemical doping induced absorption spectra for pristine P3HT film (black curve) and hybrid sample at 0° (red curve) and 90° (blue curve) polarizations. Dashed lines indicate the spectral position of far-field transmission resonances. −ΔT/T here indicates relative change of transmission spectra of the sample as in Figure 3a−c upon chemical doping.

conclude instead that the near-field coupling between the two quasi-particles induces an actual change of the polymer excited state. Even in this case, both plasmonic resonances and polymer absorption features are clearly visible in MIR far-field transmission spectra of the hybrid nanoantennas/P3HT film (Figure 5a). Doping-induced absorption spectra of pristine P3HT (black curve) and hybrid nanoantennas/P3HT probed with 0° and 90° polarized light (red and blue curves, respectively) in Figure 5b exhibit the following features: (i) broad polaron absorption, centered around 0.4 eV, similar to PIA spectra of pristine P3HT (see Figure 2b), and polarized modulations induced by resonant plasmon coupling in the hybrid sample (red and blue curves); (ii) no significant enhancement or spectral shift of the resonances induced by near-field coupling, for either of the polarizations; (iii) no enhancement of IRAV mode intensity (below 0.18 eV) in the hybrid film compared to the pristine P3HT film on either probe polarization. Features (ii) and (iii) indicate that no polarons are generated due to the coupling to surface plasmons in addition to those that are chemically induced. Therefore, we argue that the mechanism leading to enhanced polaron transitions in the presence of resonant IR nanoantennas must be dynamic and may be due to the thermal activation of polaron photoexcitation (which does not occur in the case of static, chemical doping), rather than to a purely spectroscopic effect. We emphasize that the PIA experiments involve a three-level system comprising the main excitonic transition of the polymer in resonance with the pump, as well as photoinduced polaronic transitions and nanoantenna plasmonic modes in resonance with the infrared probe; it appears that both infrared resonances must be excited simultaneously to lead to cooperative enhancement of polaronic transitions.

The generally accepted scheme for polaron photogeneration in conjugated polymers sees a competing pathway between direct photoeccitation and exciton dissociation. While the first process does not require any excess energy, the second requires thermal, photon energy, or electric field activation.41−43 Experiments clearly demonstrate that both exciton and polaron photogeneration are ultrafast (t < 100 fs) events25,44 with polaron/exciton branching ratios varying from 10% to 30% in pristine polymer films.45,46 There are two possible mechanisms by which plasmon−polaron coupling with IR nanoantennas could lead to enhanced polaron photogeneration yield: (i) formation of plasmon−polaron complexes may favor direct polaron relaxation through resonant energy transfer; (ii) absorption of IR light by the coupled resonant nanoantennas may provide excess thermal energy needed for exciton dissociation.47 Additional studies will be required to elucidate these arguments, such as “pump-push-probe” experiments48,49 or measurements of photocurrent generation in working device structures.

In conclusion, we have demonstrated, via photoinduced absorption spectroscopy, a new plasmon−polaron coupling mechanism in P3HT polymer films by engineering the plasmonic nanoantennas resonance to overlap in energy with the P3HT polaron absorption. These findings could potentially open new routes toward the design of more efficient organic photodetector and photovoltaic devices through carefully engineered metamaterials that recycle the infrared solar radiation to promote direct carrier photogeneration and exciton dissociation in polymers and donor−acceptor bulk heterojunctions.49,50 It may also be possible to engineer plasmonic nanostructures with resonances in the vis-NIR spectral region to enhance photon absorption and in the mid-IR to enhance polaron photogeneration simultaneously. Moreover, plasmon−polaron coupling demonstrated here may have further implications in functional materials other than conjugated polymers and broadly in nanophotonics. In solid-state systems, one could envision plasmonic tuning of the photogenerated polaron and bipolaron density or of photoinduced local modes of superconducting cuprates;51 in plasmonic systems, one could exploit polarons in organic semiconductors to achieve strong coupling with metamaterials52 or to design dispersion relation of propagating hybrid surface-polaron−plasmon polaritons.

ASSOCIATED CONTENT

3 Supporting Information

Experimental descriptions, IR nanoantennas fabrication methods, AFM images, more discussions of modulation features, and characterization of off-resonance sample are included. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.5b01760.

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Notes
The authors declare no competing financial interest.

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