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Ag Nanoparticle-blended Plasmonic Organic Solar Cells: Performance Enhancement or Detraction?

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ABSTRACT

The blending of metallic nanoparticles into the active layer of organic solar cells in a bid to enhance their light absorption and device performance has led to controversial reports of both efficiency enhancement and degradation. Herein, through comprehensive transient absorption spectroscopy, we present clear evidence of traps being responsible for performance degradation of poly (3-hexylthiophene): [6,6]-phenyl-C 61-butyric acid methyl ester organic photovoltaic devices incorporated with oleylamine-capped silver nanoparticles. Although the presence of the metallic nanoparticles leads to more excitons being generated in the active layer, higher losses suffered by the polaron population through trap-assisted recombination strongly limits the device performance. Device modeling based on a single mid-gap trap state introduced by the AgNPs can well reproduce the current-voltage curves of the plasmonic organic solar cells – in agreement with the transient absorption findings. These new insights into the photophysics and charge dynamics of plasmonic organic solar cells would help resolve the existing controversy and provide clear guidelines for device design and fabrication.

Keywords: plasmonics, organic photovoltaics, transient absorption, trap-assisted recombination, device model

1. INTRODUCTION

Bulk-heterojunction (BHJ) organic photovoltaic (OPV) is a highly promising candidate for sustainable energy. One of the advantages afforded by this technology is the means to fabricate devices through cheap, scalable solution processes and on flexible, light-weight substrates that has a low environmental impact. Substantial efforts have been undertaken to improve their power conversion efficiency (PCE), for example, through the synthesis of new low-bandgap polymers,^{1,2} optimization of film morphology,³ design of new device architectures⁴ etc. To date, PCEs of these organic solar cells (OSCs) approaching 10% have been reported.⁵⁻⁷ However, despite their progress, the performance of OSCs is still far below their inorganic counterparts due to the intrinsic low light absorption and poor charge carrier mobilities of organic materials. To maximize the light absorption and minimize the charge losses during extraction, optically thick yet physically thin active layer in the device is desired.⁸ From this perspective, metallic nanostructures offer an attractive solution to this problem. This can be achieved utilizing the localized surface plasmon resonance (LSPR) of the nanoparticles of size much less than the wavelength of light to concentrate light beyond the diffraction limit, yielding high local fields⁹; and/or leveraging on the high scattering efficiency near the resonance for light trapping in ultrathin active layers.⁸

In previous reports, metallic nanoparticles were introduced either within the active layers or external to them.¹⁰⁻¹⁷ In the former, the proximity of the metallic nanoparticles to the donor-acceptor groups allows the strongly confined LSPR field as well as the scattered light be utilized for enhancement of light absorption in the active layer. However, the degradation of device performance was also frequently reported, as were the successful cases.^{18, 19} Amidst these confusing reports, there is a lack of understanding in the loss mechanisms in plasmonic OSCs. Herein, we fabricate hybrid plasmonic OPV devices that are incorporated with oleylamine-capped AgNPs in the P3HT:PCBM active layer and investigate the

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photoexcitation generation and recombination using ultrafast optical spectroscopy. We find clear evidence on how the presence of AgNPs affects the exciton and polaron generation and their recombination dynamics. The increase in the P3HT exciton generation increase is attributed to the LSPR from the AgNPs. Nevertheless, the exciton relaxation dynamics remain invariant in the presence of the AgNPs. However, the polaron generation and the relaxation dynamics is found to be severely affected by the AgNPs. The excess excitons do not translate to more free polarons. Instead, many polarons are trapped by AgNPs functioning as recombination centers. The high trap-assisted recombination rate strongly limits the performance of the hybrid plasmonic OSCs. We successfully model the P3HT:PCBM device performance based on these tail-state recombination. By introducing a single mid-gap trap state from the AgNPs, we could correlate the performance of these plasmonic OSCs with the spectroscopic results.

2. METHODOLOGY

The AgNPs were synthesized through the reduction of AgNO_3 by oleylamine in refluxing 1,2-dichlorobenzene (boiling point: 181°C) following previous reported procedures.²⁰ Surface morphology of the P3HT:PCBM films were imaged using tapping mode atomic force microscopy (AFM, Asylum MFP-3D-BIO). AgNP images were taken by transmission electron microscopy (TEM, JEM-2010FEF, 200 KV).

Femtosecond transient absorption spectroscopy (fs-TAS) was performed in a non-degenerate pump-probe configuration. The pump pulses (500nm) were generated from an optical parametric amplifier (OPA) (Light Conversion TOPASTM) that was pumped by a 1 kHz regenerative amplifier (Coherent LegendTM, center wavelength: 800 nm; pulse width: 150 fs; power: 1 mJ per pulse), which was in turn seeded by an 80 MHz Coherent VitesseTM oscillator. The probe beam was a white light continuum generated from a sapphire plate using 800nm femtosecond pulses. Pump induced probe transmittance change (relative differential transmission $\Delta T/T$) was monitored using either a monochromator/PMT configuration (for visible probe range) or an IR-monochromator/InGaAs photodetector configuration (for NIR probe range). The excitation intensity was $\sim 7 \mu\text{J cm}^{-2}$ per pulse to minimize higher order effects. Nanosecond transient absorption spectroscopy was performed using an Applied Photophysics LKS.60 Nanosecond Laser Flash Photolysis Spectrometer with 500nm excitation pulses generated from a seed Nd:YAG, Q-switched laser (532 nm, 7 ns pulse width) and the probe was a 150 W Xe lamp aligned normal to the excitation source. The typical laser pump fluence used is $\sim 60 \mu\text{J cm}^{-2}$ per pulse. The data was collected in transmission geometry with the sample positioned at 45° with respect to both the excitation source and probe light.

The reference and plasmonic P3HT:PCBM devices were fabricated using well-established steps: (1) Patterned ITO glass was sonicated in DI-water, acetone and IPA for 15 mins each and then further cleaned with oxygen plasma; (2) 30 nm PEDOT:PSS hole transporting layer was spin-coated on the ITO and baked at 140°C for 10 min in inert atmosphere; (3) P3HT:PCBM with and without AgNPs was spin-coated to form a 100 nm thick active layer; different volume ratio of AgNP was used to form different concentration of AgNPs in the active layer. The highest concentration of AgNPs is 50% volume ratio, corresponding to an Ag concentration of around 0.38 mg/mL. (4) A 100 nm aluminum layer was deposited using thermal evaporation. (5) The device was baked under inert atmosphere again at 150°C to optimize the device performance. The current-voltage (I - V) characteristics of the devices under illumination and in the dark were recorded with a HP 4155 semiconductor analyzer. The cells were illuminated by an Air Mass 1.5 Global (AM 1.5 G) solar simulator (San-Ei XES-300, AAA rating) with an irradiation intensity of 1000W m^{-2} . Performance was averaged over 5 to 10 cells. The light intensity of the solar simulator was calibrated using a solarimeter with a reference silicon solar cell certified by the National Renewable Energy Laboratory (NREL).

3. RESULTS AND DISCUSSION

3.1 Morphology Characterizations

Figure 1 shows the morphology of the P3HT:PCBM films with and without AgNPs. Both RMS roughness is ~ 0.1 nm over a $5 \times 5 \mu\text{m}^2$ region. This shows that the morphology of P3HT:PCBM film is not significantly affected by the AgNPs. The average AgNP diameter is around 25 nm as measured by TEM as shown in Figure 1(b) inset.

Figure 1. AFM images of (a) the reference P3HT:PCBM film and (b) P3HT:PCBM film blended with AgNPs. The bright dots in the yellow circles are AgNPs. Inset in (b) is a TEM image of the AgNPs.

3.2 Exciton Generation and Recombination Dynamics

To probe the exciton generation and recombination dynamics, we performed fs-TAS by exciting the samples with 150 fs pulses centered at 500 nm and record the change in transmission. We monitor the ground state bleaching (GSB) at early delay times to evaluate the relative population of the photogenerated excitons in the films. The GSB, which is due to the state-filling of the excited states, is proportional to the population of the photoexcited excitons in the films.²¹ It appears in TAS as a positive signal ($\Delta T/T > 0$), i.e., an increase in the light transmission and decrease in the light absorption. At early time, for example at 1 ps delay with respect to the pump pulse, the major type of photoexcitation species is the P3HT excitons which have not dissociated into polarons so it can be used to evaluate the photogenerated exciton amount. Figure 2 (a) shows the TAS signal from 520 nm to 760 nm at 1 ps delay. The GSB of P3HT:PCBM spans from 520 nm to ~ 620 nm. Two peaks can be observed in this region, which corresponds to the 0-0 and 0-1 vibronic transitions.²² This is due to the highly crystalline P3HT domains that leads to a strong coupling of lattice phonons with the excitons.²³ Integrating the GSB signal at 1 ps from 520 nm to 620 nm shows that there is an increase of exciton generation by $\sim 39\%$ for P3HT:PCBM films with high (50% volume ratio) and by $\sim 12\%$ for P3HT:PCBM films with low concentration of AgNPs (3% volume ratio) as compared to the reference film (no AgNPs). Figure 2b shows the normalized decay transients probed at 1150 nm which is attributed to the photo-induced absorption (PIA) of the singlet excitons of P3HT.^{21, 24} The invariance of the relaxation dynamics indicates that the incorporation of the AgNPs does not affect the exciton dynamics in the P3HT:PCBM system. This is possible due to the fact that the exciton quenching rate by PCBM is much higher compared to the energy transfer rate between exciton and surface plasmon resonance.

Figure 2. (a) fs-TAS signal spanned from 520nm to 760nm probed at 1 ps delay. (b) Normalized decay of the PIA of the P3HT singlet excitons in different films probed at 1150 nm.

3.3 Polaron Generation and Recombination

The polaron generation can be evaluated at a suitably longer delay time (e.g., at 1 ns delay) such that the excitons and other short lifetime photoexcited species have recombined or dissociated. We monitor the transient absorption signal of the GSB at 1ns to evaluate the relative photogenerated polaron population. As shown in Figure 3 (a), the polaron generation does not show any obvious increase for the AgNPs blended P3HT:PCBM films as compared to the reference film.

A similar conclusion can be reached when we probe the dynamics at 1000 nm as shown in Figure 3 (b). The TA signal here originates from an overlap of the PIA from the P3HT excitons and polarons. At early times when exciton PIA dominates, higher PIA signal is observed for the hybrid plasmonic films indicating a higher exciton generation rate. After the excitons have vanished at several tens of picoseconds later, the PIA of the polarons becomes the only source of the TA signal at 1000 nm. The TA signal in this time region for the plasmonic films is not higher than the reference, indicating polaron generation is not increased in the presence of AgNPs. This implies that although we get a higher exciton population, the excitons do not efficiently form more free polarons. One possible reason can be attributed to the low exciton dissociation efficiency in the plasmonic films. However, since the exciton dynamics is almost invariant, we can exclude this reason. Another reason is that the AgNPs introduce a lot of charge traps that can localize the photogenerated polarons and act as recombination centers. It is highly possible that due to the local field enhancement, exciton generation rate is high in the vicinity of AgNPs. Hence, when they dissociate into polarons, the polarons can be rapidly trapped by the nearby AgNPs – leading to the invariance of the PIA signal at 1 ns as observed here.

Figure 3. (a) fs-TAS signal spanned from 520nm to 760nm probed at 1 ns delay. (b) The decay probed at 1000 nm which is attributed to an overlapping of PIA of the P3HT excitons and polarons.

The polaron dynamics were also investigated over longer time scales using a nanosecond transient absorption spectroscopy (ns-TAS) setup. The GSB dynamics probed at 560 nm from 1 ns to 5 μ s is displayed in Figure 4. The GSB signal can be fitted by a combination of trap-assisted recombination (generally considered to be a monomolecular process) and a higher order recombination (attributed to delayed bimolecular recombination under high fluence). The delayed bimolecular recombination is a consequence of the finite probability of delayed charge detrapping from the trap states under high fluence, where these freed charges subsequently undergo recombination with other free charges.²⁵ More details can be found in an earlier work from our group.²⁶ For the polaron recombination in the plasmonic films, we found a higher SRH like trap-assisted recombination rate in the presence of AgNPs. The recombination increases as the blended AgNP concentration in the films increases. This is consistent with the conclusion obtained from fs-TAS results.

Figure 4. GSB dynamics probed at 560nm from ns to several μ s, corresponding to the recombination of the polarons.

3.4 Plasmonic OPV Device Model

To further understand the device performance of plasmonic OPVs and correlated them to the transient spectroscopic findings, we also modeled the device current-voltage (J - V) properties by introducing a single level midgap trap from the AgNPs. Device performance of BHJ OSCs was successfully simulated with a set of coupled differential equations that include the Poisson equation and drift-diffusion equations of holes and electrons.²⁷⁻³² Under steady-state conditions, the generation and recombination of the free charge carriers reach an equilibrium. The types of recombination are of great importance in the modeling of the device performance. In many of the earlier reports, the basic type of charge carrier recombination was set as the Langevin type, i.e., recombination by two free opposite carriers upon reaching their capture radius.²⁷ However, this model fails to reproduce some experimental results such as voltage dependence of dark current density carrier concentration of such plasmonic devices – evident from the current-voltage and charge-extraction measurements.³³ By introducing an exponential distribution of tail-states that lie below the transporting level so that the recombination can happen between free charges and the charges trapped in tail states, several reports successfully modeled the device performance and explained other experimental results.^{33, 34} In this scenario, the tail states lie just below the transporting level, i.e., the edge of conduction and valence band and have an exponential distribution:

$$N_{t(e,h)}(E_{t(e,h)}) = N_{et(ht)} \Delta E \exp\left(-\frac{|E_{t(e,h)} - E_{C,V}|}{E_{et(ht)}}\right), \quad (1)$$

where $N_{et(ht)}$ is the effective electron (hole) trap density, $E_{et(ht)}$ is the electron (hole) trap characteristic energy, $E_{t(e,h)}$ is the electron (hole) trap energy level and $E_{C,V}$ is the conduction (valence) band edge. The complete equation for the recombination via tail states at the conduction (valence) band edge can be expressed as:

$$R_{et(ht)} = \int_{E_V}^{E_C} N_{et(ht)} \exp\left(-\frac{|E_{t(e,h)} - E_{C,V}|}{E_{et(ht)}}\right) \frac{C_{e(h)}^{e(e)} C_{e(h)}^{h(h)} (np - n_i^2)}{C_{e(h)}^{e(e)} (n + n_1) + C_{e(h)}^{h(h)} (p + p_1)} dE, \quad (2)$$

where $C_{e(h)}^{e(e)}, C_{e(h)}^{h(h)}$ conduction (valence) band tail electron and hole capture coefficient, respectively. $n_1 = N_C \exp((E_t - E_C) / kT)$ and $p_1 = N_V \exp((E_V - E_t) / kT)$.

From the transient absorption results, we believe the Shockley-Read-Hall (SRH)-like trap-assisted recombination dominates in the device under solar irradiation. The trap-assisted recombination takes place when a free charge carrier meets an opposite charge carrier trapped in the tail states. To reduce the number of the fitting parameters, we used a symmetric band structure as input, i.e., same density of states (DOS) in the conduction and valence bands, same tail state density and distribution below the conduction and valence bands. The generation rate was also set to be uniform across the device and independent on electric field and temperature instead of Braun-Onsager type of generation.

Based on experimental results reported elsewhere that the exciton dissociation efficiency is found to be independent of electric field and temperature in many organic photovoltaic systems,^{35, 36} Figure 5 shows the experimental and simulated results of device performance under different light intensities. Good fits to the experimental data can be obtained. Table 1 displays the parameters used in the global fitting.

Figure 5. J - V curves of the reference P3HT:PCBM devices under several different light intensities. Dots are the experimental data and lines are the simulated results.

Table 1. Parameters used in the P3HT:PCBM reference device fitting.

Parameters (unit)	Symbols	Values
Free electron mobility ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_n	2.40×10^{-7}
Free hole mobility ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$)	μ_h	2.03×10^{-7}
Effective electron/hole trap densities ($\text{m}^{-3} \text{eV}^{-1}$)	$N_{\text{et}}, N_{\text{ht}}$	1×10^{25}
Characteristic energy of electron/hole tails (meV)	$E_{\text{et}}, E_{\text{ht}}$	49
Effective density of free electron/hole states (m^{-3})	N_c, N_v	1.18×10^{26}
conduction band tail electron capture/ valence band tail hole capture coefficient (m^3/s)	C_e^e, C_h^h	7.28×10^{-15}
Conduction band tail hole capture/ valence band tail electron capture coefficient (m^3/s)	C_e^h, C_h^e	4.26×10^{-16}
Charge generation rate under 100mW/cm ² light ($\text{m}^{-3}\text{s}^{-1}$)	G_0	6.15×10^{27}
Series Resistance (Ωm^{-2})	R_s	7.15×10^{-4}

In plasmonic OPV devices, the presence of AgNPs gives rise to more traps in the active layer as observed from the TAS experiments. These subgap traps are believed to originate from the core of the AgNPs. Since Ag has a work function of around 4.5 eV which may provide a recombination center for the charge carriers in P3HT:PCBM, we introduce a single trap that is located 0.3 eV below the conduction band of P3HT:PCBM. The recombination via the AgNP trap is:

$$R_{\text{Ag}} = \frac{r_e r_h (np - n_i^2)}{r_e (n + n_1) + r_h (p + p_1)}, \quad (3)$$

where r_e and r_h is the AgNP trap capture rate of electrons and holes, respectively. r_e and r_h linearly scale with the AgNP density and electron/hole capture cross sections.

Furthermore, we consider the AgNPs lying near the electrodes may also lead to the non-ohmic contacts. Based on this reason, we also introduce an injection/extraction barrier for the plasmonic devices. Assuming that this trap density increases linearly with the concentration of the AgNPs, the plasmonic device performance was fitted. Figure 6 displays the experimental and simulated plasmonic device J - V curves with several different AgNP concentration. Table 2 lists the parameters extracted from the fittings. It is clearly seen that the trap density increases as the AgNP concentration increases. Apart from that, the extraction barrier at the contact also increases when the AgNP concentration increases. Hence, the fitted results validate that the degradation of device J - V characteristics as due to an increase in the trap density.

Figure 6. J - V curves of the reference and the plasmonic OPV devices. Dots are the experimental data and lines are the simulated results.

Table 2. Parameters used in the AgNPs blended P3HT:PCBM device fitting.

Type of Device	Electron Capture Rate (s ⁻¹)	Hole Capture Rate (s ⁻¹)	Contact Barrier (eV)
Reference device	0	0	0
Low AgNP concentration (3% vol) device	3.49×10^6	3.94×10^6	1.22×10^{-4}
Middle AgNP concentration (25% vol) device	2.79×10^7	3.15×10^7	1.72×10^{-2}
High AgNP concentration (50% vol) device	5.58×10^7	6.63×10^7	2.90×10^{-2}

4. CONCLUSION

We present a comprehensive study on the generation and recombination of the photoexcitation in P3HT: PCBM films blended with oleylamine-capped AgNPs using transient absorption spectroscopy. We find that the exciton generation increased in the presence of the AgNPs. Nevertheless, exciton recombination is negligibly affected by the AgNPs because the exciton quenching rate by PCBM is much faster than the recombination. However, polaron generation and recombination is strongly affected when AgNPs are present. The polaron population does not increase as observed from TAS at 1 ns delay; and they undergo a fast trap-assisted recombination from ns to μ s. The results clearly point to the

increased trap density introduced by the AgNPs as the culprit. From the device performance modeling, it is found that by introducing a single trap state in the device model based on exponential tail-state recombination, both the reference and the plasmonic OPV devices can be successfully simulated. These results correlate well with the transient absorption results and further validate all our findings.

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