Nanoscale

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Light concentration and redistribution in polymer solar cells by plasmonic nanoparticles

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We propose an optoelectronic model to investigate polymer solar cells with plasmonic nanoparticles. The optical properties of the plasmonic active layers, approximated by the effective medium theory, are combined with the organic semiconductor model. The simulation suggests the enhancement on short-circuit photocurrent is due to light concentration and redistribution by particle plasmons.

As a promising alternative to traditional photovoltaic devices, polymer solar cells are lightweight, flexible, inexpensive to fabricate, and tunable on the molecular level.[1,2] Although the bulk heterojunction blend has been introduced to boost the device performance, the energy conversion efficiency of polymer solar cells is still very low. There is considerable interest in improving their performance by incorporating plasmonic nanoparticles (NPs) into the active layer.[3,4] Recently, the enhancement effects of gold NPs on the photocurrent and energy conversion efficiency have been observed in experiments.[5] The pioneering research work on optical and electrical effects of gold nanoparticles in the active layer has been demonstrated.[6] In these studies, the bulk heterojunction blend can be mixed with metallic NPs and regarded as a new composite with novel optical properties. In order to optimize the fabrication of plasmonic polymer solar cells, an efficient electromagnetic model is necessary to rapidly estimate the device performance.[7–10]

In this paper, we use the effective medium theory to approximate the optical properties of active material with plasmonic nanoparticles, and combine a semiconductor model to study the short-circuit photocurrent influenced by plasmonic nanoparticles. The simulation results indicate optical absorption enhancement and light redistribution in active layers by particle plasmons. The calculated results illustrate the potential enhancement of the photocurrent and energy conversion efficiency by the plasmonic effects.

We focus on a common polymer bulk heterojunction blend poly(3-hexylthiophene):[6,6]-phenyl-C$_{61}$-butyric acid methyl ester (P3HT:PCBM).[11] The device structure is illustrated in Fig. 1 using glass, indium tin oxide (ITO), poly(3,4-ethylenedioxythiophene):poly-

(styrenesulfonate) (PEDOT:PSS), a plasmonic active layer and an aluminum back electrode. The plasmonic active layer consists of P3HT:PCBM and gold NPs. Following the experimental work in ref. 6, we carry out studies for a low concentration of gold NPs (no more than 2% volume ratio). Such a low concentration should maintain the flat morphology of the active layers in device fabrication.

First of all, we consider the optical absorption of plasmonic active layers. The transfer-matrix method based on Maxwell's equations is used to calculate the optical propagation in the multilayer structure of the polymer solar cells.[12] All refractive media are assumed to be isotropic. The sizes of nanoparticles are assumed to be much smaller than their wavelengths. The dielectric function for gold nanoparticles with a diameter of 20 nm are calculated and used in this model.[13,14] The refractive index of the plasmonic active layer that has been approximated by Bruggeman's effective medium theory depends on the volume ratio of gold NPs.[15] Fig. 2(a) shows that the pristine P3HT:PCBM bulk heterojunction has an optical absorption band edge at 650nm. It also indicates that there is significant absorption enhancement in the active layer with plasmonic NPs around the wavelength 650 nm; as the volume ratio of gold NPs increases from 0.5% to 2%, the absorption band edge extends to wavelengths longer than 650 nm and the absorption is further enhanced. The change in the absorption band edge is attributed to the absorption of the plasmonic NPs themselves. The absorption band is extended due to the average distances between gold nanoparticles getting closer to each other. The absorption enhancement originates from near-field
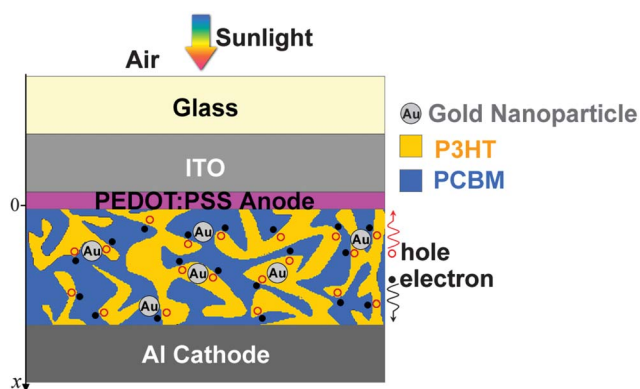
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Fig. 1 Illustration of polymer bulk heterojunction solar cells with gold nanoparticles embedded in active layers.
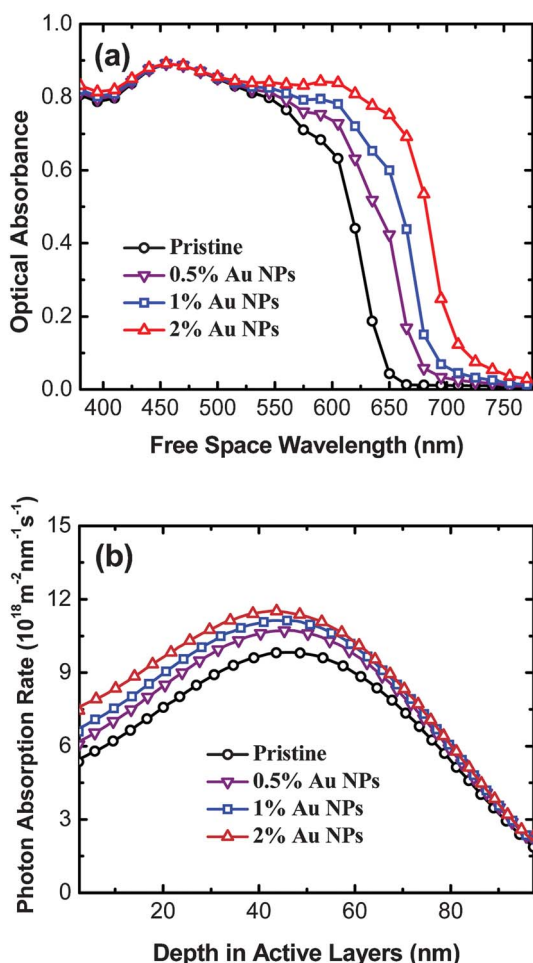
Fig. 2 (a) Optical absorbance in active layers for various volume ratios of gold NPs (100 nm ITO, 20 nm PEDOT:PSS, 100 nm active layer and 100 nm Al). (b) Profiles of photon absorption rate as a function of the depth in the 100 nm active layer.

light concentration by localized surface plasmon resonance.[13] In the dominant absorption band (below 650 nm), the particle plasmon energy could be transferred to the photon energy in bulk hetero-junction blend before it is dissipated into ohmic damping in the metal. The absorption enhancement below 650 nm can be attributed to the exciton generation in the organic semiconductor, because the absorption rate in the organic semiconductor is typically higher than the plasmon decay rate.[16] In contrast, the enhanced absorption of plasmonic active layers above 650 nm should be mainly dissipated into the plasmon damping loss of metallic NPs. This is because there is almost no absorption of P3HT:PCBM above 650 nm, and according to our previous research the gold NPs cannot act as exciton dissociation sites.[4] The results here are also consistent with our optical simulation using a 3D finite-difference time-domain method presented in ref. 13.

Using the absorption coefficient $p(\lambda,x)$, we calculate the photon absorption rate in the active layers as below,

$$G(x) = \int_{\lambda} \frac{p(\lambda,x)I_{AM1.5}(\lambda)}{\hbar \nu} d\lambda \tag{1}$$

where $I_{\mathrm{AM\ 1.5}}(\lambda)$ is the standard air mass 1.5 solar irradiance spectrum (100 mW cm^{-2}), $\hbar$ is Planck's constant, and ν is the wave frequency of

light. Since the optical energy distribution in active layers influences the performance of polymer solar cells,[17] we compare the profiles of different photon absorption rates in active layers, as seen in Fig. 2 (b). It is observed that the local photon absorption rates are increased by plasmonic NPs, with a larger increase near the hole conductor PEDOT:PSS. Typically, the holes in the active layer have a lower mobility than the electrons. The absorption enhancement effect creates more holes close to the contact where they are extracted. This reduces the number of holes that are lost during carrier transport due to bi-molecular recombination, and thus increases the photocurrent. This theoretical result could partially explain the experimental report that finds using proper metallic NPs with optimized volume ratios might facilitate hole extraction and reduce carrier recombination.[5]

Next, the profiles of photon absorption rates in plasmonic active layers are put into an electrical model. The low volume ratio of embedded gold NPs doesn't change the basic energy levels in organic semiconductors. The energy band diagram is shown in Fig. 3(a).[18] In the electrical model, the gold NPs might act as hole hopping sites, carrier recombination centers or electron scattering centers. These electrical effects have been primarily studied by C. C. D. Wang et al.[6] To exclude these possible electrical effects in our research and focus on the plasmonic light concentration and redistribution, we assume that the gold NPs are capped by an ultra-thin shell and insulated from the P3HT:PCBM, which is feasible in material engineering.[19] The device is described by using the metal–insulator–metal picture based on Koster's methods.[20] The device is thought to be made up of one semiconductor with the lowest unoccupied molecular orbital (LUMO) of the acceptor and the highest occupied molecular orbital (HOMO) of the donor as valence and conduction bands, respectively, as shown in Fig. 3(b).

In an organic semiconductor, the charge continuity equation is expressed as below,

$$-\frac{1}{q}\frac{dJ_{\mathrm{n}}(x)}{dx} + PG(x) - (1-P)R(x) = 0 \tag{2}$$

$$\frac{1}{q}\frac{dJ_{\mathrm{p}}(x)}{dx} + PG(x) - (1-P)R(x) = 0 \tag{3}$$

with q being the elementary charge, $J_{\mathrm{n}}(x)$ and $J_{\mathrm{p}}(x)$ the electron and hole current density at a depth x in the active layer, $G(x)$ the photon absorption rate, P the dissociation probability of charge carrier pair and $R(x)$ the bi-molecular recombination rate from the Langevin
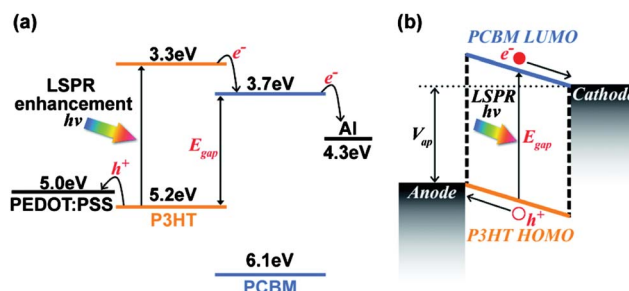

Fig. 3 (a) Schematic of the energy levels of P3HT:PCBM bulk hetero-junction. The electron and hole are transported through the respective materials and collected by the electrodes. The difference between the HOMO of P3HT and the LUMO of PCBM is E_{gap}. (b) Metal–insulator–metal model with positive applied bias V_{ap}.

model. To focus on the investigations of plasmonic effects, we assume that P is 90% on the short-circuit condition.[21,22] The Langevin recombination rate is given by

$$R(x) = [n(x)p(x) - n_i^2](\mu_n + \mu_p)q/\varepsilon_r\varepsilon_0 \qquad (4)$$

where $n(x)$, $p(x)$, n_i, μ_n, μ_p and $\varepsilon_r\varepsilon_0$ are electron density, hole density, intrinsic carrier density, electron mobility, hole mobility and spatial average static permittivity of active layer, respectively. To simplify the physical model, electron and hole mobility are assumed to be constant throughout the active layer. The value of static permittivity, electron and hole mobility are obtained from the literature.[22–24]

Incorporating both the drift and diffusion of charge carriers, we obtain the current density equations for electrons and holes, respectively. In organic semiconductor theory, the charge continuity equations are expressed as below,

$$J_n(x) = -qn(x)\mu_n E(x) + qD_n\frac{d}{dx}n(x) \qquad (5)$$

$$J_p(x) = -qp(x)\mu_p E(x) - qD_p\frac{d}{dx}p(x) \qquad (6)$$

$D_{n,p}$ are the carrier diffusion coefficients given by the Einstein relation:

$$D_{n,p} = \mu_{n,p}k_B T/q \qquad (7)$$

where k_B is the Boltzmann constant and T is the absolute temperature. The electric field distribution $E(x)$ is determined by the Poisson equation,

$$\frac{dE(x)}{dx} = \frac{q}{\varepsilon_r\varepsilon_0}[n(x) - p(x)] \qquad (8)$$

The built-in voltage V_{bi} is determined by

$$\int_0^L E(x)dx = V_{ap} - V_{bi} \qquad (9)$$

where V_{ap} is the external applied voltage and L is the thickness of the active layer.

This theoretical model is validated by comparing the simulated short-circuit photocurrent density J_{sc} with the experimental results of Li et al.,[25] as shown in the inset of Fig. 4. Our previous numerical study has suggested that it is not detrimental to the absorption of polymer solar cells when the NPs are in an appropriate low volume ratio range.[13] Fig. 4 also demonstrates that under the low volume ratio limitation, the short-circuit current density increases as the volume ratio of gold NPs increases. This is attributed to the optical absorption enhancement by particle plasmons. Within the low volume ratio range, higher volume ratios of gold NPs result in greater absorption enhancement. The theoretical simulation indicates that the short-circuit current strongly depends on the optical absorption. The localized surface plasmon resonance increases the localized optical absorption and changes the profile of the photon absorption rate in the active layers to facilitate hole extraction. The photocurrent enhancement can be attributed to the plasmonic light concentration and redistribution in the active layers.

In the future, this research can be further combined with the detailed electrical parameters of polymer solar cells from experiments
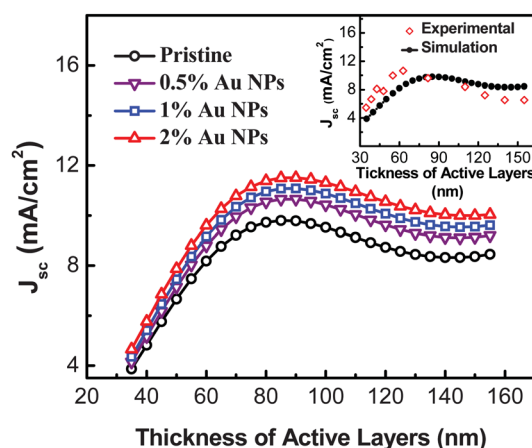

Fig. 4 Short-circuit photocurrent density J_{sc} as a function of the thickness of the active layer. The inset shows the experimental and simulated J_{sc} as a function of the thickness of the active layer.

and electrical boundary conditions at the metal–organic interface to have a more comprehensive physical understanding of plasmonic polymer solar cells.

Conclusions

We proposed an optoelectronic model to investigate plasmonic effects on the performance of organic solar cells. The effective medium theory was used to simplify the optical properties of the plasmonic active layer. The short-circuit photocurrent influenced by plasmonic NPs was considered in the model. The simulation results showed the optical absorption enhancement around the band edge of P3HT:PCBM by the embedded plasmonic NPs in the active layer. Particle plasmons concentrated and redistributed the absorbed photon energy in the active layers to facilitate hole extraction in organic semiconductors. Our results demonstrated the enhancement of the photocurrent by using plasmonic NPs. These results could provide a theoretical method to guide the design, fabrication and optimization of plasmonic polymer solar cells.

Acknowledgements

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