E-beam deposited Ag-nanoparticles plasmonic organic solar cell and its absorption enhancement analysis using FDTD-based cylindrical nano-particle optical model

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Abstract: We report the plasmon-assisted photocurrent enhancement in Ag-nanoparticles (Ag-NPs) embedded PEDOT:PSS/P3HT:PCBM organic solar cells, and systematically investigate the causes of the improved optical absorption based on a cylindrical Ag-NPs optical model which is simulated with a 3-Dimensional finite difference time domain (FDTD) method. The proposed cylindrical Ag-NPs optical model is able to explain the optical absorption enhancement by the localized surface plasmon resonance (LSPR) modes, and to provide a further understanding of Ag-NPs shape parameters which play an important role to determine the broadband absorption phenomena in plasmonic organic solar cells. A significant increase in the power conversion efficiency (PCE) of the plasmonic solar cell was experimentally observed and compared with that of the solar cells without Ag-NPs. Finally, our conclusion was made after briefly discussing the electrical effects of the fabricated plasmonic organic solar cells.

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References and links

1. Introduction

Discontinuous metal film prepared by an electron-beam deposition technique can provide an easy way to induce the localized surface plasmon resonances (LSPRs) effect into the solar cells which is originated from collective electron charge oscillations of metallic NPs or cluster surfaces embedded in a dispersive dielectric medium. Thus, such metallic inclusions in a form of NPs or nano-clusters have been a device element for constructing an efficient solar cell while overcoming weak absorption of the photo active layer, which is one of the limiting factors in the P3HT:PCBM (poly(3-hexylthiophene): [6,6]-phenyl-C61-butyric acid methyl ester) based BHJ solar cells [1–8]. It is well known that the surface plasmons (SPs) are confined light waves that can be localized (localized surface plasmon, LSP) at their interfaces. The main reason for use of LSPRs in the solar cells is due to the presence of a high electric field enhancement excited by strong SP resonances at the interface between Ag-NPs and their surrounding area, mainly, the active layer [3,7]. Therefore, extensive studies of applying LSPRs into thin film solar cells have been reported to identify its important roles depending on NPs shapes, neighbors, and their distributions [3–8]. On the other hand, it has been suggested that the electrical mechanism rather than the optical effects of metallic particles embedded organic solar cells can play an important role in the estimation of the LRSP effects to performance improvement [9] in a particular case there is no big difference in the optical absorbance of PEDOT:PSS/P3HT:PCBM polymer with and without metallic NPs.

In this letter, we have fabricated the plasmonic enhanced P3HT:PCBM bulk heterojunction solar cells using a simple electron-beam deposition technique [4]. Significantly improved photocurrent was identified experimentally, and its mechanism was analyzed by introducing a FDTD-based cylindrical Ag-NPs model, revealing that LSPRs are the main causes of the optical absorption enhancement of the solar cells. We show that this three-dimensional (3D) Ag-NPs optical model is quite useful to understand the light absorption behaviors of Ag-NPs depending on wavelengths, and shape parameters in a dispersed bulk hetero-junction (BHJ) dielectric material. We have also investigated the electrical aspects of our Ag-NPs embedded plasmonic solar cells to obtain the detailed operating mechanism, and to compare with others [8–12].

2. Device fabrication and measurements

The electron-beam deposition of pure silver metal on ITO glass was performed with a deposition rate of 0.1Å/sec. A buffer layer of poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) was spin-coated using an aqueous solution (Baytron PVP Al 4083) onto Ag-NPs/ITO glass, followed by annealing at 120°C for 15min on a hot-plate under air environment, and then the samples were transferred into a nitrogen purged glove box. The active material containing P3HT and PCBM with 1:1 weight ratio dissolved in 1,2-dichlorobenzene were spin-casted on top of the PEDOT:PSS to be ~140nm-thick, followed by annealing process at 140°C for 5min to minimize photo-oxidation. The device structures used were of glass/ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al and glass/ITO/Ag-NPs/PEDOT:PSS/P3HT:PCBM/LiF/Al as described in Ref [4]. The PEDOT:PSS layer is used for both hole transporting layer and buffer layer to prevent direct contact between NPs and P3HT:PCBM. The current density voltage characteristics were measured using a Keithley 2400 source meter and a 450W Oriel Xe lamp with AM 1.5G filter, corresponding an illumination intensity of 100mW/cm². For comparison, reference solar cells were duplicated.
by one of our authors using the same materials in order to make our experiment more accurate. After depositing Ag metal on ITO [4], the surface roughness of the substrate became heavily inhomogeneous that consists of random shapes of discontinuous islands or clusters with non-uniform diameters. As increasing their film thicknesses, their heights were ranging from a couple of nm to tens of nanometers. In this experiment, Ag deposition thicknesses of 1, 3, and 5 nm set by an e-beam deposition controller were chosen to be sufficiently thin enough to produce such randomly distributed Ag-NPs on ITO glass.

Figure 1 depicts the photocurrent-voltage characteristic of the fabricated solar cells which was conducted in a nitrogen purged glove box. Plasmonic solar cells incorporated with Ag-NPs exhibited higher efficiency of 2.75% compared to the reference cells which was 1.67%. It is note that the $J_{sc}$ was increased from 4.7 to 8.2 mA/cm$^2$, implying that the improved photocurrent was resulted from the enhanced photogeneration of excitons due to the plasmonic resonant field in the vicinity of Ag-NPs. This eventually contributes to the increase of the photocurrent. However, the open circuit voltage ($V_{oc}$) was reduced by 0.01V primary due to a decrease in work function of the transparent electrode [11].

![Fig. 1. Jsc-V curve. (a) a regular without Ag-NPs, and (b) a plasmonic solar cell with Ag-NPs of 5 nm thick.](image)

Fig. 1. $J_{sc}$-$V$ curve. (a) a regular without Ag-NPs, and (b) a plasmonic solar cell with Ag-NPs of 5 nm thick. The short-circuit current density was obviously enhanced due to the photogeneration of the increased excitons via LSPRs of Ag-NPs. Parameters such as $J_{sc}$ [mA/cm$^2$], Voc [V], FF [%], and $\eta$ [%] were estimated to be 4.7 mA/cm$^2$, 0.59V, 63.5%, and 1.67% for a regular cell, and 8.2 mA/cm$^2$, 0.58V, 58.7%, and 2.75% for a plasmonic solar cell, respectively. The active area was of 0.12 cm$^2$.

3. Optical modeling and analysis

We have examined a shape of a truncated Ag-spheroid model which was cut about one third from the top of it as shown in Fig. 2. However, this model was not fully able to explain the photocurrent enhancement because their LSPR modes were too tightly localized in the vicinity of Ag-NPs within PEDOT:PSS and ITO layer, resulting a very limited contribution to the enhancement of the optical absorption of the solar cell. We have also simulated second type of Ag-NPs having a circular shape as described in Ref [5] in which their strong resonant modes only exerted to their sides of Ag-NPs that did not increase the optical absorption and the photocurrent generation in this simulation. Therefore, we have introduced a cylindrical Ag-NPs model as shown in Fig. 3 after careful estimations of Ag-NPs dimension which was obtained from AFM images [4]. For simplicity, we assumed that the cylindrical Ag-NPs are uniformly distributed and form a mono layer on ITO glass. As a result, it was able to elucidate the optical absorption enhancement of the plasmonic solar cells even if the shape of Ag-NPs and its distributions are not identical to that of the real case. From the AFM estimation, the average size of Ag-NPs was estimated to be around 60 nm and the height of NPs to be near 20 nm (smaller sizes of Ag-NPs or clusters were ignored). Finally, an uniformly dispersed cylindrical Ag-NPs model on top of ITO was made, and mixed with PEDOT:PSS layer [4] in order to investigate the LSPR behaviors of Ag-NPs. The periodic
boundary conditions and electromagnetic (EM) symmetries imposed with perfectly matched artificial absorbing layers were utilized to simulate optical boundary conditions [5]. As shown in Fig. 3(b), the sun light is incident through the semi-infinite ITO-glass with the propagation vector \( \mathbf{k} \) normal to the surface and the electric field \( \mathbf{E} \) parallel to the surface that excites the collective oscillation modes of the electronic gas of Ag-NPs, and then the excited modes become damped by the imaginary part of the active medium, leading to optical absorption spectra appeared to be a peak and dip curve as shown in Fig. 5 and 6.

Fig. 2. A truncated spheroid FDTD model, showing excited LSPR modes that are tightly localized in the vicinity of Ag-NPs within PEDOT:PSS and ITO layers. However, this model results in very limited contribution to the optical absorption enhancement of the solar cell.

Fig. 3. Schematic diagram of proposed device model. (a) a cylindrical Ag-NPs model, (b) its cross-sectional view in which the local field intensity, \( |\mathbf{E}| \) was integrated over the volume surrounding the cylindrical Ag-NPs.
Figure 4 shows the excitation of LRSPs in the vicinity of Ag-NPs with a function of wavelengths, creating strong electric fields and evanescently propagating waves that contribute to the enhancement of the light absorption, and thus, the photocurrent of the organic solar cells. Such strong electric field are arisen from the corners of the cylindrical Ag-NPs that were also tightly confined but evanescently spreading into neighbors that can then be coupled to the photoactive absorption region [6]. After examining the electric field patterns of LRSPs with three wavelengths at the interfaces, three important facts from this device simulation were noticed. First, all the optical wavelengths do not equally participate in the increase of the optical absorbance even if exhibiting their own strong electric field resonances. For instance, at shorter wavelengths, the extending LRSPs fields tend to less propagate into the active layer. Second, the smaller sizes of Ag-NPs with less than 20nm thick are less likely to contribute to the photocurrent increase of the solar cells even if the plasmonic resonance of Ag-NPs is clearly existed (not shown here). This is because their resonant electric filed cannot exert fully to the active layer. Third, not only the strength and frequency of LRSPs depend on NPs shape factors and distributions, but also they become sensitive to changes in surrounding dielectric medium.

In order to investigate the optical absorption behaviors of Ag-NPs distributions, we separately plot the normalized light absorption of P3HT:PCBM with and without Ag-NPs as functions of its shape parameters. As increasing Ag-NPs thickness (Fig. 5(b)), as well as separation (Fig. 5(c)) and diameter (Fig. 5(d)), the resonant peak of the absorption spectra became red-shifted. It was also noted that the absorption peak with increasing the size of Ag-NPs tends to show a wide full width at half maximum, leading to more possibility of absorbing electromagnetic evanescent field by the active layer. Figure 5(a) evaluates the normalized absorbance with/without Ag-NPs as a function of wavelength near the bottom of the aluminum electrode, showing the amount of the transmitted light to the electrode is limited as increasing the Ag-NPs thickness. On the other hand, Fig. 5(b), 5(c), and 5(d) depicted the absorption enhancement spectra calculated from the active layer which is very close to the interface between Ag-NPs and the active layer (an extended area of ~10nm long from Ag-NPs) as shown in Fig. 3(b). The absorbance increases at wavelengths of 440nm~460nm, and 480nm~640nm that became a maximum value when Ag-NPs height is close to that of the PEDOT:PSS layer (Fig. 5(b)), its separation is near 100nm (Fig. 5(c)), and its diameter is near 60nm (Fig. 5(d)), respectively. There are two lobes in the normalized absorption band that can be explained by the optical constant (n, k) difference between ITO and the dispersive active layer [3]. For instance, the absorption spectra exhibits a sharp trench at $\lambda = 430nm$ which is associated with LSPR mode concentrated in the interface between metal and ITO, and the optical index difference at this wavelength is capable of spectrally...
separating out the evanescent wave into ITO layer, which is undesirable from the beneficial absorption enhancement in the organic cells [7].

From the localized region of PEDOT:PSS as shown in Fig. 3(b), the peak absorption enhancement factor [5] was calculated, showing a very high peak at the absorption edge of 630nm. The magnitude of peak enhancement factor was estimated to be ~52. This portion of absorbed photon energy will be redistributed evanescently into the active layer, and concentrated near the interface between Ag-NPs and the active layer, eventually coupling to the photoactive absorption region. Usually, the mobility of hole is less than that of electron in the active layer such that holes reach the electrode interface slower than electron. Therefore, the photon energy redistribution and concentration in the active layer close to PEDOT:PSS could benefit for more holes to be collected due to the reduced transport path of localized holes, leading to enhanced photocurrent.

Fig. 5. Normalized absorption spectra of P3HT:PCBM layer with and without Ag-NPs. (a) the total absorption of P3HT:PCBM active layer, (b)-(d) the absorption of a local region close to PEDOT:PSS layer. (a) and (b) the height of Ag-NPs was varied from H = 10, 15, to 20nm thick, while two variables such as its radius (D = 60nm) and separation (P = 100nm) were fixed. (c) D = 60 nm, H = 20 nm, and P = 50, 100, 150, 200 nm. (d) H = 20 nm, P = 100 nm, D = 20, 40, 60, 80nm, respectively.

4. Consideration of electrical aspects

The optical absorption spectra of ITO glass/Ag-NPs with and without PEDOT:PSS as a function of the Ag deposition thickness are shown in Fig. 7(a). The absorption peak corresponding to the excitation of the LSPR was red-shifted when the PEDOT:PSS layer is incorporated. The amount of optical absorbance was increased at wavelengths of 400-800nm within the absorption spectrum of the polymer in both increasing the deposition thickness of Ag metal and adding PEDOT:PSS layer. We have also observed a significant optical absorption difference of PEDOT:PSS/P3HT:PCBM thin film with and without Ag-NPs as shown in Fig. 7(b). The enhanced optical density in the spectral range of 300–650nm where the P3HT:PCBM film is highly sensitive, was due to the increased electric field in the active
region by photoexcited LSPRs around Ag-NPs. Our experimental result is exactly matched to reported publications [8,10].

Fig. 6. Normalized absorption spectra of a local region in active layer close to PEDOT:PSS in case of an arrangement pattern with p = 100nm, h = 20nm, and D = 60nm, and their broadband optical absorption enhancement spectra which was evaluated by the ratio of the field strength with Ag-NPs to that of the regular device without NPs in the wavelength range 300 nm ≤ λ ≤ 670 nm.

On the other hand, it was reported that the electrical device model rather than the optical mechanism of metallic particles embedded organic solar cells can play an important role in the performance improvement [9] in a particular case; the dispersed metallic-NPs are actually embedded within PEDOT:PSS layer, and the corresponding LSPR-enhanced electro-magnetic (EM) fields are trapped laterally. Thus there was no difference in the optical absorbance of PEDOT:PSS/P3HT:PCBM layer with and without metallic NPs. In other words, the absorption enhancement due to the incorporation of Au-NPs was insignificant and provided only minor contribution to PCE improvement. Therefore, by considering electrical model instead of optical effects, the authors in Ref [9] found that the incorporation of Au-NPs could reduce the resistance of the PEDOT:PSS layer, and increase the surface roughness of the interfacial layer between P3HT:PCBM and PEDOT:PSS, contributing to the improvement of hole collection efficiency, and eventually leading to J_{SC} and FF enhancements. Thus, we have also examined the surface morphology changes as a function of the deposition thickness of Ag metal by using an Atomic Force Microscope (AFM) and an optical microscope. In Fig. 8(a) and 8(b), it was obtained from the surface of a P3HT:PCBM BHJ solar cell without Ag-NPs. AFM figures with Ag-NPs are not provided here, but optical microscope figures are shown in Fig. 8 (c) and 8(d). We have observed that upon increasing the deposition thickness of Ag metal, the surface roughness was somewhat increased. It may be possible that this roughened surface will increase the interface area between the anode and the active medium, and provide shorter routes for holes to travel to the anode that eventually increasing J_{SC} of the solar cells. In addition, the reduced mean distance of between generated holes and the PEDOT:PSS interface diminishes the dependence of holes on the external electric field for collection at the anode, also improving the FF [9]. However, in our devices, we have identified that both V_{OC} and FF were decreased a little bit while significantly increasing the J_{SC}. Therefore, the proposed analysis provided in Ref [9], does not fully support the mechanism of the performance improvement for our experiment, implying that the increased J_{SC} may be mainly due to the LSPR effects, inducing more photogenerated charge carriers by enhanced absorption of the active layer. However, the obtained J-V curve as shown in Fig. 1 indicated that a slight reduction of the series resistance was estimated from the calculated data of ~91.2Ω for a plasmonic solar cell and ~185Ω for a regular solar cell. This implies that this factor also contributes to improve the solar cell performance to some extent. The FF decrease
in our plasmonic solar cell can be explained by Ag-NPs induced surface morphology roughness that increase the surface recombination to some extent at the interface between PEDOT:PSS and P3HT:PCBM [8]. The $V_{OC}$ was remained the same value, but the very slight decrease is attributed to lower work function caused by Ag-NPs on ITO layer [11].

Based on our experiment and theoretical modeling, we have identified that our plasmonic solar cells are highly sensitive to the incident wavelengths, and the significant change of the absorption spectra in the measurements is a direct evidence showing that the light absorption of P3HT:PCBM layer is affected by the incorporation of Ag-NPs due to the strong LSPR EM fields potentially distributed into the adjacent active layer. On the other hand, we have also carefully considered that the effect of the increased interfacial layer between PEDOT:PSS and P3HT:PCBM could contribute to the hole collection efficiency, increasing $J_{SC}$ of the solar cells due to increasing the anode surface roughness between the anode and the active layer. Therefore, we concluded that the optical effects are identified to be a major mechanism to performance improvement compared to the electrical effects, and the electrical effects stem from the roughened interface effect and a slight resistance reduction is regarded as a minor contributor to PCE improvement because the electrical model alone cannot fully support our device results; for example, a significant increase of the solar cell efficiency with a FF decrease.

Fig. 7. The optical absorption spectra of the E-beam deposited Ag-NPs and Ag-NPs/PEDOT:PSS (a), and the P3HT:PCBM/PEDOT:PSS with and without Ag-NPs (b).

Fig. 8. Atomic Force Microscopy (AFM) images of the surface of P3HT:PCBM layer; (a) and (b), and optical microscope images after completing the device fabrication process as increasing the deposition thickness of Ag-metals; (c) Ag 1nm thick and (d) Ag 7nm thick.
5. Conclusion

In conclusion, we have demonstrated an increased optical absorption of an organic BHJ solar cell that utilizes the LRPRs of Ag-NPs, and performed a device simulation to interpret the photocurrent enhancement mechanism via a 3-D cylindrical Ag-NPs FDTD model. The solar cell efficiency was increased as a function of Ag-NPs thickness, and at a thickness of 50Å, a 60% increase of the PCE was achieved compared to a cell that does not have Ag-NPs. Therefore, the experimental and simulation results implied that the strong optical field intensity associated with a LSPR is responsible for enhanced exciton generation near the interface of Ag-NPs/PEDOT:PSS and the active layer. Finally, we have also discussed the electrical aspects of the fabricated plasmonic organic solar cells.

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