

Dependence of the Device Performance of Polymer Solar Cells on the Insertion of Metal Nanoparticle Layers at the Electron-collecting Electrodes

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ABSTRACT

We report a study of the dependence of the device performance of polymer solar cells with the blend films of regioregular poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl C₆₁-butyric acid methyl ester (PCBM) on the insertion of a layer of metal (Pd, Ag, Cu or Au) nanoparticles (NPs) at the electron-collecting electrodes. The short-circuit current density, the incident photo-to-current conversion efficiency, and the power conversion efficiency of the cells increased by the insertion of metal-NPs; the insertion of the Pd-NP layer has a large enhancement effect for the device performance. The light absorption was found to increase by forming the Pd-NP layer on the blend film without changing the light reflection. The formation of Au NPs on the blend films was directly observed by scanning tunneling microscopy (STM). The possible mechanism for such improvement is discussed using the results of the solar-cell parameters and the STM.

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Keywords : Polymer Solar Cells, Metal Nanoparticles

1. Introduction

Organic photovoltaic devices based on conjugated polymers are a promising alternative source of electrical energy, and have been investigated by many different methods with the aim of improving the performance of these devices.^{1–11} In particular, the devices containing blend films of regioregular poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl C₆₁-butyric acid methyl ester (PCBM) have been widely studied, and have exhibited a high power conversion efficiency (PCE), almost 7.0%.⁸ During the preparation of the P3HT:PCBM active layer, the mixed phase spontaneously segregates into interpenetrated domains, creating bulk heterojunction (BHJ) devices.⁵ For organic solar cells, the enhancement of the PCE by the incorporation of a nanotextured Au layer at the electron-collecting electrodes has been reported.¹² The previous work has reported that the PCE increases because of the improvement in the short-circuit current density (J_{sc}).¹² Such improvement has been explained by localized surface plasmon resonance (LSPR) within the Au nanoparticles (NPs).¹² The excitation of the LSPR within metal NPs is known to create strong near-field electromagnetic fields, which enhances the light absorption and the photocurrent of organic photovoltaic devices.^{13–19} However, the effects of metal NPs other than Au on the characteristics of organic solar cells have not yet been fully investigated. The research is an interesting issue because various metal NPs have the ability to enhance the performance of organic solar cells.

Here we report the study of the dependence of the J_{sc} , the PCE, and the incident photo-to-current conversion efficiency (IPCE) of the P3HT:PCBM BHJ photovoltaic cells on the insertions of Pd-, Ag- or Cu-NP layer in addition to the Au-NP layer at the electron-collecting electrodes. The absorption enhancement of the blend films without changing the light reflection has been demonstrated. This enhancement is thought to contribute to the enhancement of the J_{sc}

and the IPCE of the P3HT:PCBM solar cells. The shapes of metal NPs on the blend films were observed with a scanning tunneling microscopy (STM) technique, which showed metal NPs with various dimensions.

2. Experimental

Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) films of around 30 nm thickness were obtained by spin-coating an aqueous solution (Baytron PVP AL 4083) on indium tin oxide (ITO)-coated glass substrates, followed by annealing at 135°C for 10 min under the ambient atmosphere to form the hole-collecting layers. Solutions containing P3HT and PCBM dissolved in chlorobenzene (1.4 wt%) or dichlorobenzene (2.5 wt%) with a mass ratio of 1:0.8 were spin-coated at 1000 or 2000 rpm on the top of the PEDOT:PSS films to form the blend films of around 80 nm thickness. Then, metal NPs (Pd, Au, Ag or Cu), LiF, and Al layers were thermally deposited onto the P3HT:PCBM blend films to form the electron-collecting electrodes. Finally, the devices were annealed at 135°C for 8 min or 25 min under an Ar gas atmosphere. The nominal thickness of the metal-NP layers of 1.2 nm was adopted to follow the reported ratio of the film thickness of Au-NP to that of LiF.¹² The fabricated device structure was ITO/PEDOT:PSS/P3HT:PCBM/metal-NPs (1.2 nm)/LiF (0.4 nm)/Al. The active area was 0.04 cm². Current density–voltage (J - V) curves were measured under simulated solar irradiation (100 mW/cm², AM 1.5 G).

3. Results and Discussion

The J - V characteristics of the P3HT:PCBM polymer solar cells without and with the Pd-, Ag-, Cu- or Au-NP layer are shown in Fig. 1, where an ITO layer is the hole-collecting electrode. An increase in the J_{sc} was clearly observed for the polymer solar cells

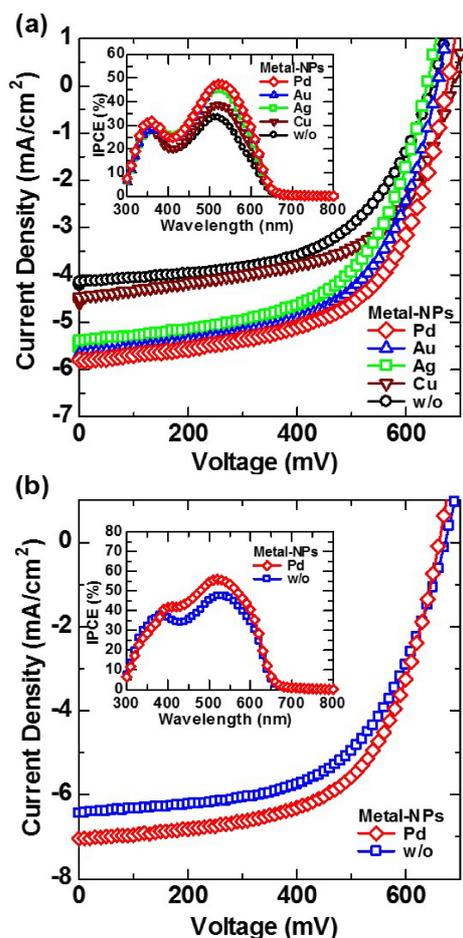


Figure 1. (Color online) J - V characteristics (main panel) and IPCE characteristics (inset) of ITO/PEDOT:PSS/P3HT:PCBM/metal-NPs/LiF/Al. (a) These devices were fabricated with chlorobenzene (1.4 wt%), 1000 rpm spin-coating, and an 8 min annealing time. (b) These devices were fabricated with dichlorobenzene (2.5 wt%), 2000 rpm spin-coating, and a 25 min annealing time.

Table 1. Solar cell parameters of the devices without and with the metal-NP layer (Pd, Ag, Cu or Au). For the fabrication (a), these devices were fabricated with chlorobenzene (1.4 wt%), 1000 rpm spin-coating, and an 8 min annealing time. For the fabrication (b), these devices were fabricated with chlorobenzene (2.5 wt%), 2000 rpm spin-coating, and a 25 min annealing time.

Fabrication	Metal NPs	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF	PCE (%)	Improved PCE
(a)	w/o	4.14	640	0.57	1.51	±0%
(a)	Cu	4.47	680	0.57	1.73	0.22%
(a)	Ag	5.40	630	0.59	1.99	0.48%
(a)	Au	5.67	650	0.59	2.16	0.65%
(a)	Pd	5.80	670	0.59	2.30	0.79%
(b)	w/o	6.44	670	0.58	2.49	±0%
(b)	Pd	7.05	660	0.60	2.78	0.29%

with the Pd-, Ag-, Cu- or Au-NP layer. Table 1 shows the solar cell parameters of the devices without and with the metal NP layer for the J_{sc} , the open-circuit density (V_{oc}), the fill factor (FF), the PCE, and the improved PCE. We confirm that the device performance improves by the insertion of the Au-NP layer, which is consistent with that of the previous work.¹² In the current study, in particular, the J_{sc} largely increased for the polymer solar cells with the Pd-NP

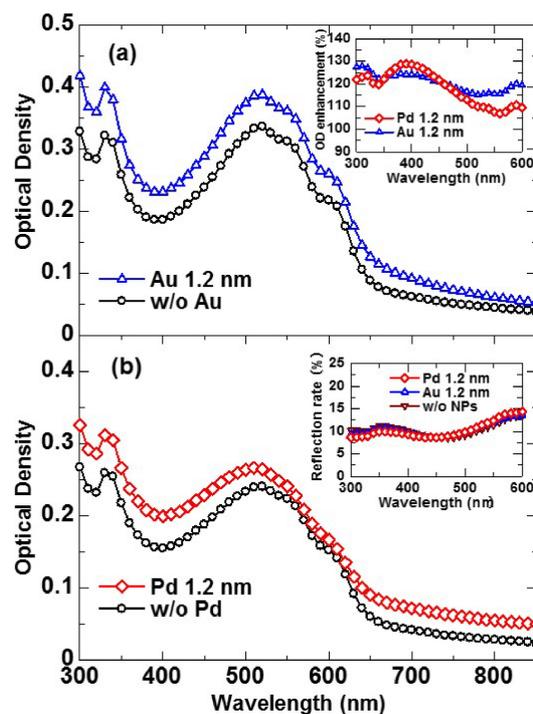


Figure 2. (Color online) (a) Absorption spectra of quartz/P3HT:PCBM/Au-NPs (1.2 nm) and quartz/P3HT:PCBM. The inset shows the enhancement ratio of the absorption spectra of quartz/P3HT:PCBM/Au-NPs (1.2 nm) to that of quartz/P3HT:PCBM. (b) Absorption spectra of quartz/P3HT:PCBM/Pd-NPs (1.2 nm) and quartz/P3HT:PCBM. The inset shows the reflection rate of quartz/P3HT:PCBM/metal-NPs (Pd or Au 1.2 nm) and quartz/P3HT:PCBM.

layer, which showed the PCE of 2.78%. The performance improvements using the metal NPs/LiF/Al structures under thermal annealing conditions were observed for the polymer solar cells with various metal-NP layers. The insets of Fig. 1(a) and 1(b) show the IPCE characteristics of the polymer solar cells without and with the Pd-, Ag-, Cu- or Au-NP layer. The IPCE characteristics of the cells with the metal-NP layer were improved compared with that of the cells without the metal-NP layer.

To investigate the reason for the variation of the J - V and the IPCE characteristics, we measured the light absorption of the BHJ blend films without and with the metal-NP layer. Since it is difficult to discuss the difference of the light absorption between the blend films due to the variation of the film thickness, we used the same blend film to evaluate the differential absorption for studying the effect of the metal NP layer. First, we measured the absorption of the P3HT:PCBM blend film on quartz substrates. Then, we fabricated the metal-NP layers on the top of the same blend film and measured the light absorption. As a result, we were able to reduce the ambiguity of the light absorption due to the difference in the film thickness. As shown in Fig. 2, the absorption of the blend films was increased with the metal-NP layer (Pd or Au). The result for the Au case is consistent with that of the previous study.¹² The inset of Fig. 2(a) shows the enhancement ratio of the absorption of the blend films with the Pd- or Au-NP layer. This enhancement ratio was obtained from the ratio of the absorption of the blend films with the metal-NP layer to that without the metal-NP layer. To examine the influence of the light reflection on the absorption, we measured the reflection rate of the blend films without and with the Pd- or Au-NP layer (see the inset of Fig. 2(b)). This result confirms almost no difference between the reflection rates of the blend films without and with the metal-NP layer. Thus, we demonstrate that the absorption enhancement is not caused by the effect of the reflection from the metal-NP layers.

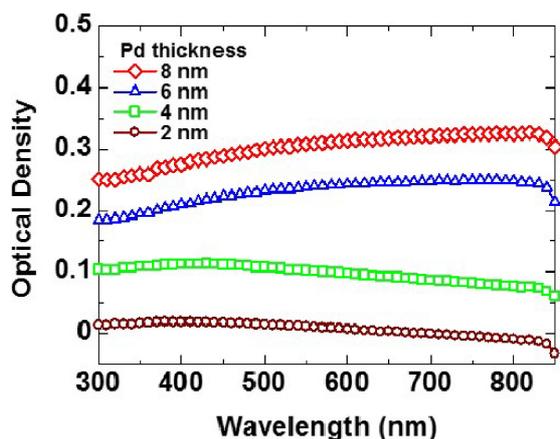


Figure 3. (Color online) Dependence of the absorption of quartz/Pd-NPs on the nominal thickness of the Pd-NP layer.

To study the absorption of the metal-NP layers themselves, we fabricated the samples with the structure of quartz substrate/Pd (2–8 nm) and measured their absorption. As shown in Fig. 3, the absorption increased as the nominal Pd thickness increased. Almost no clear peak in the absorption spectra was observed. This result is inconsistent with that of the previous study using the Au-NP layer, where the peak in the absorption spectra was observed and the maximum peak position in the absorption spectra shifted toward longer wavelengths with increasing the nominal Au thickness.¹²

It has been reported that both the shape and the size of metal NPs are key factors to determine the intensity and the wavelength region of LSPR.^{12,17,20} However, the surface morphology of metal NPs on blend films has not yet been fully investigated.¹² Thus, it is an interesting issue to observe the shape and the size of metal NPs; we measured them using a STM technique. The STM measurements were performed under high vacuum conditions below 5×10^{-8} Pa. Figure 4(a) shows the height image of STM of the surface of the blend film with the Au-NP layer on the film under an applied voltage $V = 3$ V at a current $I = 100$ pA. Since the aggregated clusters in the blend film look like particles, we could not determine the sites of metal NPs using only the STM image. Thus, we performed scanning tunneling spectroscopy (STS) measurements. Figure 4(b) shows the current image of STM of the same film at $V = -1.2$ V, which were obtained by measuring the STS characteristics (see Fig. 4(c)) for each region. As shown in Fig. 4(c), the STS characteristics for the region marked with the pink square in Figs. 4(a) and 4(b) showed semiconducting characteristics. This behavior was only observed using the blend films. However, the STS characteristics for the region marked with the blue square in Figs. 4(a) and 4(b) showed metallic characteristics. This behavior could not be observed using only blend films. The regions with a red color in Fig. 4(b) show a high current at $V = -1.2$ V. From the current image of STM, the existence of metal NPs with a size of several to a few tens nanometers is observed. Thus, this result confirms that the surface of the blend film is not completely covered with the Au metal. Further studies for the surface morphology of other metal (Pd, Ag and Cu) NPs and for the depth profiles of metal NPs penetrating into the blend films are interesting issues because the difference of the distribution states between metal NPs may cause the difference of the solar-cell parameters mentioned above, which will be reported in a separate paper.

We now turn to a discussion of the origin of the variation of the device performance using the metal-NP layers. As discussed in the previous work,¹² the LSPR effect may possibly enhance the light absorption of the blend films. The LSPR should have an effect at a particular wavelength in the absorption and the IPCE spectra, depending on the type of metal and the NP dimensions.¹⁷ However, we did not observe such clear enhancement at a particular

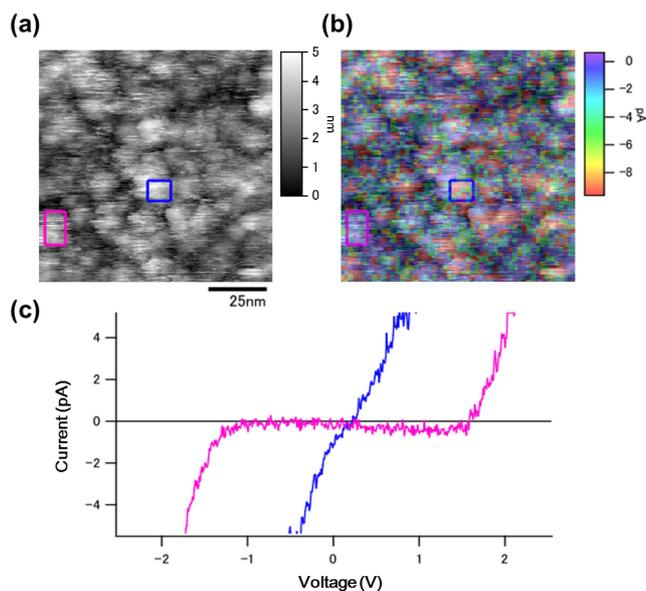


Figure 4. (Color online) (a) The height image of scanning tunneling microscopy (STM) and (b) the current image of STM of the sample surface of ITO/PEDOT:PSS/P3HT:PCBM/Au-NPs (1.2 nm). The regions with a red color show a high current. (c) Scanning tunneling spectroscopy (STS) characteristics of the regions marked by pink and blue squares in Figs. 4(a) and 4(b).

wavelength for the cells with the Pd- or Au-NP layer in the present study (see the insets of Fig. 1, the inset of Fig. 2(a), and Fig. 3). This result means that the formation of the Au-NPs confirmed by the STM study do not cause the LSPR effect. Thus, the origin of the enhancement is unlikely due to the LSPR effects in the case with the Pd-NP layer.

Another possible origin of the variation of the device performance is due to the suppression of the formation of PCBM radical anions at the interface of the electron-collecting electrode LiF/Al.²¹ The thermal annealing for polymer solar cells with a structure of ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al after the deposition of Al electrode (a post-annealing treatment) has an effect to form the PCBM⁻Li⁺ charge-transfer complexes due to the electron transfer from LiF/Al to PCBM through a reaction of $3\text{PCBM} + 3\text{LiF} + \text{Al} \rightarrow 3\text{PCBM}^-\text{Li}^+ + \text{AlF}_3$.^{22,23} The formation has been directly observed using electron spin resonance (ESR) spectroscopy.²¹ The formation of the complexes causes the electron scattering at the PCBM/LiF/Al interfaces, and decreases the J_{sc} .²¹ When the metal-NP layer is inserted between the layers of P3HT:PCBM and LiF/Al, the metal-NP layer may suppress the electron doping to PCBM due to the electron transfer from Al to metal, not to PCBM. This explanation is consistent with the observation of the highest device performance using the Pd-NP layer because Pd has a large work function (5.44 eV) and may attract electrons from Al.²⁴ Also, the highest device performance of the cells with the Pd-NP layer may be explained by the large surface segregation of PCBM at the electron-collecting electrode due to the post-annealing treatment of the cells because Pd has larger surface energy than that of other metals (Au, Ag, Cu) and electrode materials (Al, LiF);^{25–27} the surface energy of metals (Pd, Au, Ag, Cu) is larger than that of the electrode materials (Al, LiF).^{26,27} The suppression of the PCBM⁻Li⁺ complexes and/or the large surface energy of metals may enhance the J_{sc} due to the decrease in the electron scattering and/or the large surface segregation of PCBM at the LiF/Al interfaces. The larger surface energy of metals (Pd, Au, Ag, Cu) than that of the electrode materials (Al, LiF) causes the larger surface segregation of PCBM at the electron-collecting electrode, which may explain the slight increase in the FF for the devices with the metal NPs due to the reduction of the charge-

carrier recombination. Further experiments using ESR spectroscopy to clarify the mechanisms of the variation of the device performance are currently in progress, and will be reported in a separate paper.

4. Conclusions

We studied the effects of metal NPs (Pd, Au, Ag, Cu) on the device performance using the polymer solar cells of ITO/PEDOT:PSS/P3HT:PCBM/metal-NPs/LiF/Al, and found that the metal NPs vary the device performance. The polymer solar cells with the Pd-NP layer performed better than those with other metal-NP layers. The origin of the enhancement of the device performance was discussed considering the effects of LSPR, the formation of the PCBM⁻Li⁺ charge-transfer complexes, and the surface segregation of PCBM due to the different surface energy of metals (Pd, Au, Ag, Cu). The detailed mechanisms of the variation of the device performance are interesting issues, which would be clarified by further experiments using ESR spectroscopy from a microscopic viewpoints.

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