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Effective and tunable light trapping in bulk heterojunction organic solar cells by employing Au-Ag alloy nanoparticles

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Effective and tunable light trapping in organic solar cells (OSCs) has been demonstrated by employing Au-Ag alloy nanoparticles (NPs). A simple vacuum thermal annealing method has been employed to fabricate the Au-Ag alloy NPs with tunable molar ratio, and thereafter tunable localized surface plasmon resonance (LSPR). The incorporation of the alloy NPs with an appropriate molar ratio into the OSCs structures supports amplification of the electric field near the particles surface through LSPR and results in an enhanced light absorption at the absorption wavelength region of the absorber owing to the near field coupling. The short-circuit photocurrent density of the alloy NPs-based OSCs is improved from 7.37 to 8.74 mA/cm² compared to that of control OSCs, and the efficiency of 3.03% is obtained, which corresponds to an enhancement factor of 19%. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4898137]

Organic solar cells (OSCs) offer great technological potential as renewable energy sources because of the cheap and easy processing technology, mechanical flexibility, and low weight.^{1,2} The efficiency is still needed to be improved for commercial applications. The conflict between the need of thick active layer to ensure sufficient photon absorption and maintaining thin film due to the relatively low carrier mobility and short exciton diffusion length of organic materials is one of the main obstacles for the efficiency enhancement.3-5 Various light trapping approaches have been explored to solve this problem by increasing the absorption of the active layer. Among them, surface plasmon resonance (SPR) excited by metallic nanostructures has been demonstrated effective in light trapping without increasing the physical thickness of the active layer.^{6,7} Coupling of nanostructures with thin film technology has been played important role in optoelectronic devices,^{8,9} and metallic nanoparticles (NPs) have become popular and extensively nanostructures for absorption enhancement in OSCs.¹⁰⁻¹⁴ The incorporation of metallic NPs into the OSC structures supports amplification of the electric field near the particles surface through localized SPR (LSPR) and could result in enhanced light absorption owing to the near-field coupling.

Au and Ag NPs have been studied in great detail in the OSCs due to their relative strong scattering efficiency, broad LSPR absorption band in the visible range, and chemical stability.^{15,16} Mixing of the Au and Ag NPs has also been investigated in OSCs, which result in larger efficiency enhancement due to a dual resonance enhancement.¹⁷ Compared to monometallic NPs and physical mixing of the Au and Ag NPs, the Au-Ag alloy NPs have more advantages due to the potential to combine the best of both metals in terms of plasmonic properties and exhibit unique electronic, optical, and catalytic properties that distinct from those of

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: jingfeng@jlu.edu.cn and hbsun@jlu.edu.cn. the corresponding monometallic particles.^{18–21} Moreover, Au and Ag easily form alloys for different compositions with very little surface segregation due to their similar lattice constants, 4.08 Å and 4.09 Å, respectively.²² Different from the monometallic NPs, for which both shape and size of the metallic NPs are key factors determining the LSPR wavelength,²³ the LSPR can be tuned easily to the desired spectral range by varying the molar ratio of the Au-Ag alloy NPs. Therefore, the use of the Au-Ag alloy NPs in the OSCs offers great potential for effective and tunable light trapping, and more attention should be paid to its applications in the OSCs.

Both wet chemically synthesis and thermal annealing methods have been employed to fabricate the metallic particles. The particles can be directly deposited on the ITO anode by the thermal annealing process, which is more favorable for its application in the OSCs. However, it is not easy to control the size and shape of the NPs compared to that fabricated by the wet chemically synthesis, which results in a limit in tuning the LSPR wavelength. In this work, the thermal annealing method has been employed to fabricate the Au-Ag alloy NPs with tunable molar ratio and its effect on light trapping in the OSCs has been investigated. The Au-Ag alloy NPs were obtained by a co-evaporation of Au and Ag onto the ITO substrate and followed by the thermally annealing process, so that the molar ratio of the alloy NPs can be easily and precisely tuned by controlling the evaporation rate of the Au and Ag individually. Light absorption enhancement in the active layer has been obtained by strong LSPR excited at the absorption wavelength region of the absorber by the alloy NPs with an appropriate molar ratio. Meanwhile, light scattering from the NPs elongates the optical path length which contribute to the light absorption enhancement at a shorter wavelength. The short-circuit photocurrent density (Jsc) of the alloy NPs based OSCs is improved from 7.37 to 8.74 mA/ cm², and the efficiency of 3.03% is obtained, which corresponds to an enhancement factor of 19%.

The Au-Ag alloy NPs embedded in the OSCs are prepared by co-evaporating Au and Ag with 1 nm of thickness on the ITO/glass substrates in the evaporation chamber and then thermally annealed at 400 °C for 1 h in the vacuum environment. During the heating process, the thin metal films break up under surface tension to form isolated particles, and the size and shape of which are sensitively dependent on the surface conditions of the underlying layer.²⁴ In case of the Au or Ag monometallic NPs, the Au or Ag film with the same thickness of 1 nm was evaporated onto the ITO/glass substrate and then annealed under same condition. The morphologies of the metallic nanoparticles on the substrates were characterized by a field emission scanning electron microscope (SEM, JSM-7500F, JEOL, Japan).

The interface between the electrode and the organic active layer of OSCs plays an important role in the carrier collection and interfacial resistance. A poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) layer $(\sim 20 \text{ nm})$ is spin-coated onto the NPs as a hole transport layer while also as a buffer layer to avoid exciton annihilation due to direct contact between the metallic NPs and active layer. Subsequently, a solution of poly (3-hexylthiophene-2, 5-diyl) (P3HT) and (6, 6)-phenyl-C61 butyric acid methyl ester (PCBM) (1:0.8) in chloroform with a concentration of 1 wt. % was spin-cast on top of the PEDOT:PSS layer. The resulting film with a thickness of 100 nm was annealed at 150 °C for 30 min. For all the devices, a bi-layer cathode of Ca/Ag (2/100 nm) was thermally deposited under high vacuum (5 \times 10⁻⁴ Pa). The active surface area of the device was 10 mm². The OSCs with Au or Ag monometallic NPs and without the NPs were also fabricated on the ITO/ glass substrates for comparison. The thickness of each layer was monitored by quartz crystals and calibrated by a Spectroscopic Ellipsometers (J. A. Woollam Co., Inc., USA). The photovoltaic characteristics of the device were measured with a 1 sun simulated AM 1.5G illumination with a light intensity of 100 mW/cm^2 and a Keithley 2400 sourcemeter. The absorption spectra of the samples were measured by a UV-vis spectrophotometer (UV-2550, SHIMADZU Co., Inc., Japan).

The SEM images of pure Au, Ag, and Au-Ag alloy NPs with a molar ratio of 0.377:0.623 on the ITO/glass substrates are shown in Figs. 1(a)-1(c). The molar ratio for the Au_{0.377}Ag_{0.623} alloy NPs was determined by the evaporation rate of the Au and Ag and further confirmed by the X-ray Photoemission Spectroscopy (XPS) (Fig. 2(d)). The molar ratio calculated from the XPS is 0.3997:0.6003, which exhibits no much deviation from that determined by the evaporation rate. The alloy NPs exhibit a much more homogeneous size distribution and spatial distribution compared to that of the Au or Ag NPs. The average size of the alloy NPs is determined to be 19 nm from statistical distribution. Both the size and the separation of the alloy NPs are between that of the monometallic NPs. In contrast, the Au NPs are small and dense, while the Ag NPs are large and sparse.

The SEM images of the Au-Ag alloy NPs with different mole ratio are shown in Fig. 2. Tunable LSPR can be observed in Fig. 2(f) by comparing the absorption spectra of the Au-Ag alloy NPs with the different molar ratio. The pure Au NPs show a characteristic peak at 552 nm, and the pure Ag NPs show a characteristic peak at 464 nm. It is known that a physical mixture of monometallic Au and Ag NPs has two absorption peaks due to the SPR of the Au and Ag, respectively.²⁵ No shift of the SPP peak positions could be observed by changing the physical mixing ratio, except the relative intensity of the two peaks. Core-shell NPs would



FIG. 1. SEM images of the metallic NPs of (a) Au; (b) Ag; and (c) Au-Ag alloy NPs formed by vacuum annealing on the ITO substrates. The scale bar is 100 nm. (d) XPS spectra of Au 4f and Ag 3d of NPs formed on the ITO substrates.



FIG. 2. SEM images of Au-Ag alloy NPs with various molar ratios of (a) Au_{0.166}Ag_{0.834}; (b) Au_{0.227}Ag_{0.773}; (c) Au_{0.377}Ag_{0.623}; (d) Au_{0.548}Ag_{0.452}; and (e) Au_{0.642}Ag_{0.358}. The scale bar is 50 nm. (f) UV/vis absorption spectra of Au and Ag monometallic NPs and Au-Ag alloy NPs with various molar ratios.

also exhibit the same two absorption peaks.^{26,27} While, only one SPR band was observed for the alloy NPs with different molar ratio, and the absorption maximum is always located between the SPR of the monometallic Ag and Au NPs. Moreover, the SPR peaks exhibit linear redshift with the increase of the Au content, which is in agreement with the theoretical predictions in the previous papers based on the Mie theory.^{26,28} The presence of only one LSPR peak and its shift with the different molar ratio both clearly confirms the formation of Au-Ag alloy NPs with homogeneous compositions.

The consistence of the SPR wavelength with the absorption region of the P3HT absorber is crucial for the absorption enhancement. To distinguish clearly the peaks position of the LSPR supported by the NPs in the OSCs, the absorption measurement has been performed for the structure of ITO/ NPs/PEDOT:PSS/P3HT:PCBM. The same structure without the NPs was used as the reference sample for the absorption measurement to exclude the absorption by the organic films at the observed wavelength region, so that the peaks originated from the LSPR supported by the NPs could be distinguished clearly. The absorption spectra for the structure with the monometallic and alloy NPs are shown in Fig. 3(a). The absorption peaks are located at 465 and 600 nm for the Ag and Au NPs case, respectively. The SPR of the monometallic NPs shows obvious deviation from the main absorption band of the P3HT absorber. The alloy NPs with various Au mole fractions of 0.166, 0.377, and 0.642 are corresponding to an absorption peak at around 500, 520, and 560 nm, respectively. Obviously, the SPR peak of 520 nm for the alloy NPs with the molar ratio of 0.377:0.623 almost coincides with the absorption peak of the P3HT absorber. Moreover, it exhibits a broad absorption spectrum covering the wavelength range from 450 to 650 nm, which is consistent with the absorption region of the P3HT absorber. Therefore, the molar ratio of 0.377:0.623 for the Au-Ag alloy NPs is appropriate for the efficient light trapping in the P3HT:PCBM based OSCs.

The effect of the NPs induced absorption enhancement is confirmed by further comparing the absorption spectra of the OSC structure employing the Au-Ag alloy NPs with the molar ratio of 0.377:0.623 as well as that without any NPs. As can be seen in Fig. 3(b), broadband absorption enhancement can be observed for the structure with the alloy NPs, which corresponds to the intrinsic absorption of P3HT. The NPs are embedded in the PEDOT:PSS film with a thickness of around 20 nm. Taking into account that the diameter of the NPs is also around 20 nm, the LSPR field may extend to the active layer. Therefore, we can conclude that the



FIG. 3. (a) The normalized absorption spectra for the OSC structure with the different molar ratio of the alloy NPs and monometallic NPs by using the same OSC structure without the NPs as a reference sample. (b) Optical absorption spectra for the OSC structure with the $Au_{0.377}Ag_{0.623}$ alloy NPs and without the NPs.

excitation of the LSPR with the favorite resonant wavelength supported by the Au-Ag alloy NPs results in the increase in the absorption of the OSCs.

The current density-voltage (J-V) characteristics of the OSCs with the Au_{0.377}Ag_{0.623} alloy NPs and without any NPs are compared and shown in Figure 4(a). A summary of their performance including the open-circuit voltage (Voc), short circuit current (Jsc), fill factors (FF), and power conversion efficiency (PCE) of the devices is given in Table I. Voc depends on the charge-transfer interaction between polymer and fullerene as well as on the HOMO-LUMO energy gap of the electrodes.²⁹ The Voc of the OSCs with and without the NPs remains constant, which means that the addition of the NPs does not reduce charge-transfer interaction. Their FF is also comparable to each other. While in case of the Jsc, the OSCs with the alloy NPs show an obviously enhancement. The Jsc of the control device is 7.37 mA/cm^2 and it is increased to 8.74 mA/cm^2 for the OSCs with the alloy NPs corresponds to an enhancement of 18.5% which compared to that of control OSCs. The increase in the Jsc can be attributed to the increased photon absorption due to the LSPR-induced light trapping. The optimized OSCs without the NPs show a PCE of 2.54%. While, in case of the OSCs with the Au_{0.377}Ag_{0.623} alloy NPs, the PCE is



FIG. 4. (a) J-V characteristics and (b) IPCE characteristic spectra of the OSCs with the $Au_{0.377}Ag_{0.623}$ alloy NPs and without the NPs.

enhanced to 3.03%, which corresponds to an enhancement of 19%.

The absorption enhancement due to the LSPR induced light trapping is further verified by comparing the measured monochromatic incident photon to electron conversion efficiency (IPCE) spectra of the OSCs with and without the Au_{0.377}Ag_{0.623} alloy NPs as shown in Fig. 4(b). The shape of the IPCE curve is highly dependent on the absorption curve of the active layer. The IPCE shows a wide band improvement from 400 nm to 570 nm for the alloy NPs-based OSCs, covers the absorption region of the P3HT, and can be attributed to the LSPR-induced field enhancement. Meanwhile, the enhancement of IPCE at around 350 nm is attributed to the elongated optical path of the incident light scattering by the NPs, which can be observed in the absorption spectra (Fig. 3).

In summary, we demonstrated an effective and tunable light trapping in the OSCs by employing Au-Ag alloy NPs.

TABLE I. Photovoltaic parameters of the OSCs with or without NPs incorporated under AM 1.5G illumination at 100 mW/cm².

Cell device	$V_{oc}(V)$	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
w-o NPs device	0.62	7.37	55	2.54
Au _{0.377} Ag _{0.623} NPs device	0.62	8.74	55	3.03

A simple thermal annealing method has been employed to fabricate the Au-Ag alloy NPs with tunable molar ratio and its effect on light trapping in the OSCs has been investigated. The Au-Ag alloy NPs were obtained by a co-evaporation of Au and Ag onto the ITO substrate and followed by the thermally annealing process, so that the molar ratio of the alloy NPs can be easily and precisely tuned by controlling the evaporation rate of the Au and Ag individually. Light absorption enhancement in the active layer has been obtained by strong LSPR excited at the absorption wavelength region of the alloy NPs with an appropriate molar ratio. The Jsc of the alloy NPs-based OSCs is improved from 7.37 to 8.74 mA/cm², and an enhancement factor of 19% for the efficiency has been obtained.

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