Device performance of inverted polymer solar cells with AgSiO₂ nanoparticles in active layer

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Abstract: Localized surface plasmon mediated polymer solar cells (PSCs) were fabricated using the Ag/SiO₂ nanoparticles (NPs). The inverted PSC structure without poly (3,4-ethylenedioxythiophene polystyrene sulfonate (PEDOT:PSS) was prepared due to the efficient insertion of Ag/SiO₂ NPs in the vicinity of active layer, which led to an enhancement in photoconversion efficiency (PCE). This enhancement mainly comes from the light scattering by the SiO₂ shell and the localized surface plasmon effect by the Ag core, but we also considered the structural issues such as the NP distribution, the swelling of the active layer and of the metal electrode.

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1. Introduction

Plasmonic effects due to metallic nanoparticles (NPs) are of great interest to applications in various fields, such as sensors, light-emitting diodes (LEDs) and polymer solar cells (PSCs) [1–3]. Under the influence of light free electrons collectively oscillate in metallic NPs producing strong resonant bands in absorption and scattering, which is known as the localized surface plasmons (LSP) resonance. The frequency of the electromagnetic field corresponding to LSP depends on the metal type, size, shape, and surrounding materials [4]. The LSP is associated with a strong electric field that can interact with molecules and semiconductors producing remarkable changes in spontaneous emission and in absorption. This provides the basis of using LSPs in enhancing the performance of LEDs and solar cells. For blue and green wavelength regions, respectively, Ag and Au NPs are commonly used to enhance the performance of LEDs and PSCs [5–7]. In LED applications, LSPs on metallic NPs create an efficient alternative route for electron-hole recombination suppressing the negative impact of non-radiative recombination. In PSC applications, the metallic NPs contribute to enhanced light absorption [3]. The advantages of enhancing the light absorption by metallic NPs in PSCs are quite important because, in these devices, there is always a trade-off between the light absorption and efficient charge collection for charge carriers generated by light [3]. Since the carrier transport distance in PSCs is limited and it is typically around 200 nm, only the charge generated by light at that depth can be effectively collected, while the carriers generated at greater depth are lost to efficient conversion of light into current or voltage. The metallic NPs strongly absorb in the UV-Vis region, which could be useful for better light harvesting. Moreover, these NPs can provide an efficient pathway for transporting of carriers at the interfaces between the hole- and electron transport layers and the active layer [3, 8].

However, the metallic NPs are easily oxidized under ambient conditions. Besides, for NPs located too closely to the active region serious quenching can be occurred owing to strong tunneling between the adjacent NPs in a very high fringe electric field of LSP [2, 9, 10]. In order to suppress both the oxidation and the excessive dissipation losses in metallic NPs, it has been suggested to protect the metallic cores with dense dielectric shells in core/shell structures. For the core/shell structure, various structures such as Ag/SiO2, Au/SiO2, Au/TiO2 and Au/SnO2 were suggested. The reports published in the literature indicate that the metal core induced the LSP effect and the insulating barrier provided good dispersion of NPs [11].
carrier transportation as well as light absorption [12, 13]. Moreover, it can provide the high thermal, structural and optical stability of LEDs and PSVs with such core/shell NP LSPs [2, 9–11, 14]. However, another concern is the total thickness of the active and carrier transport layers in PSCs. In conventional PSC structures, the thin layer with thickness of around 150 nm is produced by spin-coating. However, the diameter of core/shell NPs to be embedded in this layer is around 60 nm, and it can affect the quality of the interface and the surface properties of the spin-coated layer in conventional PSCs. If the NPs are introduced into the active or carrier transport layers from a solvent this can have detrimental effect on the interface quality and surface properties of the films. In order to avoid such detrimental effects dry coating process was used [15].

Hence, the inverted PSC structure with embedded Ag/SiO$_2$ is hereby proposed. The inverted PSC consisting of an active layer without PEDOT:PSS can minimize the adverse effects produced at the surface and interface [16]. In order to prevent the oxidation and excessive quenching losses in metallic NPs, the synthesized Ag/SiO$_2$ NPs were used. The Ag/SiO$_2$ NPs were embedded in the top, bottom and center of the active layer in PSCs and the performances of these 3 types of PSCs were studied.

2. Experimental procedure

The Ag/SiO$_2$ core/shell NPs were synthesized using a sol-gel method [2]. A typical preparation procedure is as follows. First, a 500 mL beaker was filled with 180 mL of aqueous solution including CTAB (0.145 g) under vigorous magnetic stirring. Next, a prepared aqueous solution of silver nitrate (0.1 M, 10 mL) was added to the mixed solution. And then, 20 mL of ascorbic acid (0.1 M) in aqueous solution was added to the mixture solution slowly within 5 min. After the mixture was further stirred for 10 min, sodium hydroxide (0.1 M) was added to accelerate the chemical reaction and the pH of the mixed solution was set at about 5. Subsequently, 50 mL of ethanol and, for the case of Ag/SiO$_2$ NPs, 1, 0.5 or 0.2 mL of tetraethoxysilane (TEOS), which controls the SiO$_2$ thickness, was added into the above-mentioned silver colloids. The solution was stirred for three more hours at room temperature (RT). After that, the Ag/SiO$_2$ NPs were washed in acetone and ethanol mixture (1:1) by centrifuge process, and finally the ethanol based Ag/SiO$_2$ NPs with the density of around 10$^{21}$/ml were synthesized.

All photovoltaic cells were prepared on a commercial indium tin oxide (ITO)-coated glass substrate. Prior to use, the patterned ITO-covered glass substrates were cleaned with deionized water, acetone, and isopropyl alcohol by ultrasonication, followed by treatment with a UV–ozone cleaner for 20 min. ZnO precursor was prepared by dissolving zinc acetate (Aldrich, 99.9%, 1 g) and ethanolamine (Aldrich, 99.5%, 0.28 g) in 2-methoxyethanol (Aldrich, 99.8%, 10 mL) under stirring for 12 h in the air [17]. The ZnO precursor solution was then spin-coated (3500 rpm, 40 s) with a thickness of 30 nm and dried at 200 $^\circ$C for 10 min in air.

For the reference sample, blends of P3HT (4002-E, Rieke Metals) and PC61BM (PCBM, Nano-C) with 1:1 weight ratio were dissolved in chlorobenzene (CB) with a concentration of 30 mg/mL, filtered through a 0.5 $\mu$m poly(tetrafluoroethylene) (PTFE) filter, and subsequently spin-coated at 600 rpm for 40 s onto the ZnO layer on ITO. The P3HT:PCBM blend films were thermally annealed at 120 $^\circ$C for 20 min. The thickness for P3HT:PCBM (active layer) blend based film was measured to be 150 nm by surface profiler (Alpha-Step D-100, KLA Tencor). For the type I sample, the Ag/SiO$_2$ NPs were coated on ZnO layer by drop-casting before coating the active layer. For the type II sample, the Ag/SiO$_2$ NPs were coated on active layer by drop-casting. In order to make the Ag/SiO$_2$ mixed P3HT:PCBM blend (type III), Ag/SiO$_2$ NPs were cleaned in acetone by centrifuge process and the ethanol solvent was changed to CB base to mix the Ag/SiO$_2$ NPs and P3HT:PCBM blend. The blend of P3HT:PCBM was dissolved in the pure CB with 80% and CB based Ag/SiO$_2$ with 20%. After that, all samples were dried in sealed petri dishes for 8 hrs under nitrogen in the glovebox. The devices were completed by depositing a 10 nm layer of MoO$_3$ and a 100 nm layer of Ag. These layers were thermally evaporated at a pressure of 1 $\times$ 10$^{-6}$ Torr through a
shadow mask. The active area of every device was around 0.37 cm$^2$. The current density–voltage (J–V) characteristics of the photovoltaic devices were measured with a Keithley 2400 source-measure unit in the dark and under 100 mW/cm$^2$ AM 1.5G condition with a solar simulator (300 W, Newport, USA), calibrated with a monocrystalline silicon solar cell as the standard PV reference (2 × 2 cm, monocrystalline silicon solar cell, calibrated at NREL, Colorado, USA).

3. Results and discussions

| NPs      | Device | Voc (V) | Jsc (mA/cm$^2$) | FF (%) | PCE (%) | Rs (Ωcm$^2$) | Rsh (Ωcm$^2$) |
|----------|--------|---------|-----------------|--------|---------|-------------|---------------|
| Ag/SiO$_2$ | Type I | 0.58    | 9.63            | 65.87  | 3.66    | 4           | 114           |
|          | Type II| 0.58    | 9.54            | 60.52  | 3.38    | 413         | 262           |
|          | Type III| 0.61   | 9.72            | 66.50  | 3.94    | 4           | 209           |
| SiO$_2$  | Type I | 0.58    | 8.30            | 57.85  | 2.78    | 4           | 112           |
|          | Type III| 0.61   | 9.18            | 61.58  | 3.45    | 6           | 193           |
| Reference|        | 0.61    | 9.26            | 65.50  | 3.69    | 5           | 217           |

It is known that the absorption intensity of PSCs located within the near field region of localized surface plasmons (LSPs) in metallic NPs can be enhanced. The silver NPs have a LSP spectrum in the blue wavelength region and it can help to absorb the light in device. The increased absorption by Ag NPs can induce the carrier generation in active layer and then the device efficiency can be enhanced [2]. Here, the excited electrons and holes in active layer should be transferred to their respective electrodes without recombination. However, the excited electrons of Ag NP surface may directly transfer to active layer in the vicinity of the Ag NPs, providing a path for excitation from the lowest unoccupied molecular orbital (LUMO) to highest occupied molecular orbital (HOMO) of the excited electrons [9]. This is a parasitic energy loss in terms of production of electron-hole pairs and their separation in the active layer. Thus, too intimate contact between the metal core of the LSP NP and the active layer has to be avoided.

In that sense the SiO$_2$ shell serves as a very useful buffer suppressing this parasitic loss mechanism [9, 10]. The authors reported an increase in light scattering and enhanced device efficiency owing to the presence of the SiO$_2$ shell. The core/shell structure can be well-controlled by chemical synthesis method and we prepared the Ag/SiO$_2$ NPs with Ag diameter
of about 25 nm and SiO₂ shell thickness of around 18 nm. The UV-Vis spectrum of the Ag/SiO₂ NP solution is shown in Fig. 1 and the TEM image of Ag/SiO₂ NPs is shown in the inset. The synthesized Ag NPs were spherical and the SiO₂ shell completely coated the Ag NPs.

In order to investigate the device performance, the Ag/SiO₂ and SiO₂ NPs were embedded in devices and four structures were fabricated: the reference sample consisting of Ag/MoO₃/active layer/ZnO/ITO/glass stack, referred to as type I sample in what follows (NPs in this arrangement were placed on top of the ZnO film), type II sample (NPs placed on top of the active layer) and type III samples (NPs placed inside the active layer), as shown in Fig. 2. The effects of these arrangements on device parameters are illustrated by Table 1. The Ag/SiO₂ embedded structures showed the enhanced short-circuit-current density (Jsc) and resulted in the enhanced fill factor (FF) performance (type I and III). However, when considering other factors, such as the surface roughness, resistance and swelling by NP insertion considered, the Ag/SiO₂ embedded type III sample showed a higher performance than the reference sample.

In case of type I sample, the Ag/SiO₂ NPs were coated on ZnO layer by drop-casting and then annealed on hot-plate at 200 °C for 5 min in air. The density of Ag/SiO₂ NPs on ZnO layer was around 8.125 × 10¹⁰/cm². The Ag/SiO₂ NPs were uniformly distributed on ZnO layer, and then the active layer and the metal electrode were deposited on it. Compared to the reference device, the Jsc of type I was enhanced by 4%, as shown in Fig. 3 (a). This enhanced current density is owing to the light absorption and scattering by inserted Ag/SiO₂ NPs. Usually the Ag/SiO₂ NPs embedded devices show a broader absorption and higher quantum efficiency in the wavelength range of 300-650 nm as compared to the Ag NPs embedded devices [9, 10]. The LSP due to the Ag core and light scattering by SiO₂ shell caused the broad spectrum with high intensity. The enhanced external quantum efficiency (EQE) of the type I sample in Fig. 3 (b) as compared to the reference sample is in good agreement with the previous report by Choi et al. in [10]. The Voc was slightly decreased due to lower shunt resistance (Rsh) that is related with charge recombination [18]. The rough surface of the Ag/SiO₂ NPs coated ZnO layer would be induced to increase the charge recombination between ZnO and active layer and decreased the Rsh [19].
In case of type II sample, the Ag/SiO₂ NPs were coated on active layer by drop-casting. Contrary to the type I sample, the active layer of type II showed a hydrophobic property in ethanol based Ag/SiO₂ NPs. This hydrophobic property induces the non-uniform distribution with the coffee-ring patterns, as illustrated by Fig. 4 (a-c). The result was a poor performance (in FF and open-circuit voltage (Voc)) of the type II sample. Among the problems encountered in this approach one can point to the swelling of the active layer during the Ag/SiO₂ drop-casting in Fig. 4 (d), the aggregation of Ag/SiO₂ NPs and the formation of non-uniform 2-3-stack layers (Fig. 4 (e)). This resulted in the metal electrode not forming a continuous layer (Fig. 4 (f)). Especially, the series resistance (Rs) and charge recombination between the cathode and the active layer can be increased due to the surface roughness and discontinuous electrode, as shown in Table I [20, 21]. Hence, the Voc of NP coated structure was decreased, which limited the device performance. Based on these results, the active layer can be adversely influenced by NP drop-casting and alternative techniques such as the dry transfer process should be employed [15].

In the case of type III sample, the Ag/SiO₂ NPs were mixed with CB and active materials. The type III sample showed the best device efficiency in this study. Compared to the reference sample, the Jsc was increased from 9.26 mA to 9.72 mA because the embedded Ag/SiO₂ NPs enhanced the light absorption and scattering in active layer. At that, the Voc of type III was not changed, which means that in the mixed structure the interface between the

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**Fig. 3.** J-V characteristics (a) and external quantum efficiency (b) of reference, type I, type II, and type III.

**Fig. 4.** Photograph (a) of Ag/SiO₂ NPs on active layer and SEM images (b, c) showing the Ag/SiO₂ NP distribution, optical microscopy image (d) of Ag/SiO₂ NPs on active layer and SEM images of Ag/SiO₂ NPs before Ag coating (e) and after Ag coating (f).

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electrode and the active layer has not been affected [9, 10]. Consequently, the type III sample showed a higher PCE performance with enhancement of 7% compared to the reference structure, as shown in Table 1.

![Graph showing external quantum efficiency and J-V characteristics of SiO2 NPs embedded device](image)

**Fig. 5.** External quantum efficiency (a) and J-V characteristics (b) of the SiO2 NPs embedded device (based on type I and III samples); The absorbance spectra of SiO2 and Ag/SiO2 NPs (c).

The LSP effects of type I, II and III samples were clearly seen in the EQE spectra (Fig. 3 (b)). The enhancement in the blue wavelength region could be related to the LSP effect due to the Ag core and the behavior in the longer wavelength region could be related to the light scattering by the SiO2 shell [9]. Indeed, the red-shift of EQE spectra in the longer wavelength region was observed for all Ag/SiO2 NPs embedded samples (Fig. 3 (b)). In contrast, the samples embedded with only SiO2 NPs showed a slight decrease of EQE with no significant shifts in the spectral position of the peaks in the blue and red regions, which indicates the leading role of additional scattering in this case (see Fig. 5). Hence, we assume that the observed spectral shift in the longer wavelength region could be caused by the Ag core. According to the report by Jankovic et al. in [14], the EQE enhancement in PSC spectrally matches the absorption spectra of NPs, but the authors point out that the oscillation mode (longitudinal and transverse) of nanostructures should be considered. Another possibility is that the observed deviation is caused by the non-uniform distribution and distance of NPs in PSC. The coated and mixed Ag/SiO2 NPs were not well-dispersed in the active layer, even though they do form a monolayer. Local variations in the NP distribution can broaden the spectrum and shift it towards the longer wavelength [22]. Though the oscillation mode and the spatial distribution of NPs quantitatively explain the observed spectra shifts of EQE in the Ag/SiO2 NPs embedded samples, further investigation for detail analysis is required.

However, the point is that the advantages of samples with Ag/SiO2 NPs as compared to the reference and SiO2 embedded sample have been clearly demonstrated in this study. Specifically, the Ag/SiO2 NPs embedded devices showed a higher efficiency than the reference or the SiO2 NPs embedded devices. This demonstrates a close interrelation between the enhanced absorbance due to NPs and the enhanced EQE by the presence of LSPs. However, the result depends very sensitively on the interface roughness caused by inserting...
the NPs, on the ability to form the continuous electrode film, on insulating properties of the SiO$_2$ shell, on filtering method and other factors. The detailed analysis of the morphology changes caused by inserting NPs, of the effects of density and arrangement of the NPs on the strength of the LSP coupling are currently under investigation and further optimization of the structure is under way.

4. Conclusions

We have presented the Ag/SiO$_2$ NPs embedded inverted PSC devices. The Ag/SiO$_2$ NPs were coated on ZnO, on the active layer and mixed into the active layer, respectively. The Ag/SiO$_2$ NPs strongly contribute to the enhanced absorption in the blue wavelength region, which is conducive to the carrier generation in the active layer. The Ag/SiO$_2$ NPs embedded device showed the enhanced performance. However, the introduction of NPs can cause certain problems, such as the non-uniform coating of the NPs, the aggregation of the NPs in the active layer, the swelling of the active layer during drop-casting, the interface roughness and breaking down of the continuous electrode film. Consequently, our results indicate that the LSP of Ag/SiO$_2$ NPs has a beneficial effect on the device performance, but the process should be carefully optimized to obtain the enhanced performance.

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