



# Plasmonic-enhanced polymer solar cells with high efficiency by addition of silver nanoparticles of different sizes in different layers

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## Abstract

This article described a dual plasmonic effect on improving the performance of polymer solar cells (PSCs). We blended respectively silver nanoparticles (AgNPs) of different sizes into the anode buffer layer and the active layer to trigger localized surface plasmon resonance (LSPR), which enhanced the broadband absorption of the PSCs. We adopted double anode buffer layers to reduce the surface roughness of the composite buffer layer, which ensured the electrical properties of the PSCs. Finally, we led to the realization of a polymer solar cell with a power conversion efficiency of 9.2%, accounting for a 21.7% enhancement as compared to pre-optimized control PSCs. These results suggest a new approach to achieve higher overall enhancement through the cooperative plasmonic effect aroused from dual resonance enhancement of two different nanoparticles.

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**Keywords:** Polymer solar cells; Silver nanoparticles; Different sizes; Double anode buffer layers; Plasmonic effect

## 1. Introduction

Polymer solar cells (PSCs) based on polymer-fullerene bulk heterojunctions (BHJs) have attracted a lot of interest due to their many advantages, including low cost, light weight, mechanical flexibility, semi-transparency and solution roll to roll processability (Chen et al., 2010; Park et al., 2009; Li et al., 2012). Multifarious efforts have been made in the past decades for the development of high-efficiency PSCs, such as rational designs of low-bandgap conjugated polymers (Jo et al., 2009; Son et al., 2013; Dou et al., 2013),

control of film morphology (Ye et al., 2012), interface engineering (He et al., 2011; Roy et al., 2009), and device fabrication processes (Ko et al., 2009). Although the efforts have led to BHJ solar cells with power conversion efficiencies (PCEs) over 9% in single-junction devices, further improvement is still necessary for commercialization.

The overall efficiency of a PSC device is governed by its internal quantum efficiency and absorption efficiency (Jo et al., 2009; Schilinsky et al., 2002). The former can approach 100% by optimizing the exciton diffusion and dissociation in the donor–acceptor BHJ and charge collection at the electrode contacts (Park et al., 2009). Therefore, absorption efficiency of incoming light in these devices becomes one of the major limitations toward improving

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PCEs. Different approaches were taken to enhance the light absorption without increasing the thickness of the active layer, so to avoid the increase in charge recombination, due to the low carrier mobilities and short exciton diffusion lengths of organic materials (Atwater and Polman, 2010). Recently, metallic nanoparticles (NPs) were introduced into PSCs for highly improved light trapping by utilizing the localized surface plasmonic resonances (LSPR) of metallic NPs (Lu et al., 2013; Li et al., 2013; Wu et al., 2012). The excitation of LSPR can be achieved when the frequency of the incident light matches its resonance peak, resulting in a strong near-field around the interface between the dielectric and metallic nanoparticles (NPs) (Wang et al., 2011; Choi et al., 2013). As demonstrated previously, the resonance peak of LSPR depends strongly on the size, shape, and the dielectric environment of the metallic NPs (Schuller et al., 2010).

However, to the best of our knowledge, the highest PCE is lower than 9% reported to date in plasmonic PSCs using metal NPs (Table 1). In this paper, we achieved a high PCE of 9.2% for our BHJ PSCs incorporating a blend of poly{[4,8-bis-(2-ethyl-hexyl-thiophene-5-yl)-benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]-alt-[2-(2'-ethyl-hexanoyl)-thieno[3,4-b]thiophene-4,6-diyl]}(PBDTTT-C-T) and [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM). We blended respectively silver nanoparticles (AgNPs) of different sizes into the anode buffer layer and the active layer to trigger localized surface plasmon resonance (LSPR), which enhanced the broadband absorption of the PSCs. To reduce the surface roughness of the composite buffer layer (PEDOT:AgNPs), the double anode buffer layers were applied to this paper, which ensured the electrical properties of the PSCs. Short-circuit photocurrent density ( $J_{sc}$ ) and PCE of our optimized PSC were respectively enhanced 11.3% and 21.7%, as compared to pre-optimized control PSCs. These results suggest a new approach to achieve higher overall enhancement through the cooperative plasmonic effect aroused from dual resonance enhancement of two nanoparticles of different sizes.

## 2. Experimental

### 2.1. Materials

The PEDOT:PSS (Baytron 4083) was purchased from Heraeus. The AgNPs (10 mg/ml in isopropanol) with a size of 20 nm were purchased from ColdStonnes Technology

(China). PBDTTT-C-T was purchased from Solarmer Materials Inc., PC<sub>71</sub>BM was purchased from ADS. DIO(1,8-diiodooctane) was purchased from TCI. The AgNPs (10 mg/ml in chloroform) with a size of 7 nm were purchased from ColdStonnes Technology (China).

### 2.2. Devices fabrication

Polymer solar cell devices based on PBDTTT-C-T:PC<sub>71</sub>BM. The concentration of the PBDTTT-C-T:PC<sub>71</sub>BM (1:1.5, weight ratio) blend solution used to form the active layer by spin-coating was 10 mg mL<sup>-1</sup> (according to the polymer weight). Chlorobenzene was used as the solvent and 3% (v/v) DIO was used as an additive to improve photovoltaic performance. Then the AgNPs were added to the solutions by weight ratios of 0.5 wt%, 1 wt%, and 2 wt%.

Devices were fabricated with the structure ITO/PEDOT:PSS with AgNPs/PEDOT:PSS/PBDTTT-C-T:PC<sub>71</sub>BM with or without AgNPs/Ca/Al. The ITO (Indium Tin Oxide) glass substrate (8Ω/□) cleaned stepwise in water, alcohol, acetone and isopropanol under sonication for 10 min for each and exposed to ultraviolet ozone (UVO) irradiation for 20 min. To prepare the double anode buffer layers, AgNPs solution were blended into the PEDOT:PSS (Baytron 4083) solution, PEDOT:AgNPs (v/v, 2:1, 3:1 or 6:1) were first spin-coated at a rate of 3500 rpm onto ITO substrates and annealed at 130 °C for 20 min in nitrogen-filled glovebox. To reduce the surface roughness of the PEDOT:AgNPs buffer layer, an additional thinner layer of PEDOT:PSS was spin-coated as a capping layer at a rate of 3500 rpm and annealed at 130 °C for 20 min. The thickness of the double anode buffer layers was ca. 60 nm. Then, the PBDTTT-C-T:PC<sub>71</sub>BM solution with or without AgNPs was spin-coated at 900 rpm on top of PEDOT:PSS layer, the thickness of the active layer was ca. 110 nm. Incorporation of AgNPs does not alter the PBDTTT-C-T:PC<sub>71</sub>BM film thickness. Finally, Ca (20 nm) and Al (100 nm) were sequentially thermal evaporated at a pressure of ca. 3 × 10<sup>-4</sup> Pa onto the active layer as a cathode. The device area, defined through a shadow mask, was 0.04 cm<sup>2</sup>.

### 2.3. Characterization of solar cells and thin films

The  $J$ - $V$  characteristics of the devices were measured using a Keithley 2400 source measure unit. The photocurrent response was obtained under 1-sun, AM

Table 1  
Previously reported plasmonic PSCs.

Plasmonic materials	Active layer	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF (%)	PCE (%)	Reference
Ag NPs + Ag nanoprisms	P3HT:PC <sub>60</sub> BM	10.61	0.64	63	4.30	Li et al. (2013)
Ag NPs + Au NPs	P3HT:PC <sub>60</sub> BM	12.21	0.63	62	4.73	Chen et al. (2012)
Ag cluster	PCDTBT:PC <sub>70</sub> BM	11.61	0.86	69	7.10	Wang et al. (2011)
Au NPs + Ag nanograting	PBDTTT-C-T: PC <sub>70</sub> BM	18.39	0.76	63	8.79	Li et al. (2012)
Au NPs + Ag NPs	PTB7:PC <sub>70</sub> BM	17.70	0.71	69	8.69	Lu et al. (2013)
Ag @ SiO <sub>2</sub>	PTB7:PC <sub>70</sub> BM	16.77	0.76	70	8.92	Choi et al. (2013)

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