



Plasmon-enhanced optical absorption and photocurrent in organic bulk heterojunction photovoltaic devices using self-assembled layer of silver nanoparticles

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ABSTRACT

Improved optical absorption and photocurrent for polythiophene–fullerene bulk heterojunction photovoltaic devices is demonstrated using a unique self-assembled monolayer of Ag nanoparticles formed from a colloidal solution. With the presence of suitable nanoparticle organic capping groups that inhibit its propensity to agglomerate, the particle-to-particle spacing can be tailored. Transmission electron microscopy reveals the self-assembled Ag nanospheres are highly uniform with an average diameter of ~ 4 nm and controllable particle-to-particle spacing. The localized surface plasmon resonance peak is ~ 465 nm with a narrow full width at half maximum (95 nm). In the spectral range of 350–650 nm, where the organic bulk heterojunction photoactive film absorbs, an enhanced optical absorption is observed due to the increased electric field in the photoactive layer by excited localized surface plasmons within the Ag nanospheres. Under the short-circuit condition, the induced photocurrent efficiency (IPCE) measurement demonstrates that the maximum IPCE increased to $\sim 51.6\%$ at 500 nm for the experimental devices with the self-assembled layer of Ag nanoparticles, while the IPCE of the reference devices without the plasmon-active Ag nanoparticles is $\sim 45.7\%$ at 480 nm. For the experimental devices under air mass 1.5 global filtered illuminations with incident intensity of 100 mW/cm², the increased short-circuit current density is observed due to the enhancement of the photogeneration of excitons near the plasmon resonance of the Ag nanoparticles.

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1. Introduction

Key advantages of organic photovoltaic (PV) technology are that organic based PV versus traditional inorganic semiconductors are inherently inexpensive; typically have very high optical absorption coefficients ($\geq 10^5$ cm⁻¹); are compatible with large area and flexible substrates [1–3]; and can be fabricated using high-throughput low temperature processes for low-cost roll-to-

roll manufacturing [4–7]. Although the efficiency of organic solar cells has improved to ~ 3 –5% [8–10], the overall performance of organic solar cells is not yet high enough for commercial opportunities. In addition low stability and degradation of organic PV devices are required to be improved [11].

In order to improve the efficiency of organic solar cells, one approach, addressed in this paper, will be to yield increased optical absorption and photocurrent generation in the photoactive layer over a broad range of visible wavelengths by inducing surface plasmons through careful control of metallic nanoparticle's properties. It is well known that the optical absorption spectra of metal nanoparticles are dominated by surface plasmons [12]. With incident light, the surface charges of metallic nanoparticles interact with the electromagnetic field, leading to an electric field enhancement that can then be coupled to the photoactive absorption region. It has been extensively studied that surface plasmons can be tuned by changing the size, shape, particle material, substrates and overcoating of the metal particles [13–15].

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The application of plasmonic materials to various PV devices has been widely utilized for improving the PV device performance [16–28]. Recently, Morfa et al. [21] reported an improved efficiency (η_{eff}) from $\sim 1.3\%$ to $\sim 2.2\%$ using surface plasmon-active Ag nanoparticle layers on indium-tin oxide (ITO) anode in poly(3-hexylthiophene) (P3HT) and phenyl-C₆₁-butyric-acid-methyl ester (PCBM) bulk heterojunction solar cell. In their study, an enhanced short-circuit current density (J_{sc}) is reported due to the increased optical absorption from surface plasmons. However, these Ag nanoparticles were actually random shapes formed during the early stages of electron-beam evaporation, forming a discontinuous Ag film of small islands with non-uniform diameters distributed on the ITO anode. As a result, their particle size and shape varied over a wide distribution which could distort the plasmonic effects by broadening their spectral enhancement [29]. Sundararajan et al. also showed that nanoparticle aggregates on the active area of the silicon diode can lead to suppression of photocurrent [30]. Yoon and Berger further showed that self-assembled Ag nanoparticles introduced a beneficial intermediate energy step which is between the anode electrode and the hole transporting layer to suppress phonon losses [31].

Recently various approaches to implementing a controlled surface plasmon-active Ag film onto organic solar cells have been introduced as random Ag nanohole films or periodic Ag nanocavity array [22,32]. However, it is still difficult to achieve controllable dimensions of nanoparticles (holes) size with a correspondingly tight distribution.

In this work, a unique colloidal Ag nanoparticle solution with the presence of suitable organic capping groups that stabilize the nanoparticles and inhibit their propensity to agglomerate is applied to organic bulk heterojunction PV devices. An improved optical absorption and photocurrent for PV devices is demonstrated due to the increased electric field in the photoactive layer by excited localized surface plasmons of Ag nanoparticles.

2. Experiments

The ITO-coated glass substrates were ultrasonicated in acetone and isopropyl alcohol, dried with nitrogen, and subsequently dried overnight in air before device fabrication. The substrates were next spin-cast using poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) (Baytron[®] P, standard grade, HC Stark) after passing through a 0.45 μm filter. The substrates were then annealed at 140 $^{\circ}\text{C}$ for 10 min in air with a resulting thickness of 40 ± 2 nm. Thicknesses were each confirmed by ellipsometry and surface profilometry for PEDOT:PSS/Si and PEDOT:PSS/ITO/glass, respectively.

The colloid was prepared from an organic salt of Ag with toluene as the carrier liquid. The salt was decomposed under controlled condition resulting in formation of Ag nanoparticles. The nanoparticles were capped by carboxylic ligand. The Ag colloidal solution was then spin-cast atop the ITO-coated glass substrate. The substrates were then annealed at 140 $^{\circ}\text{C}$ for 10 min in air and then transferred into an inert glove box environment with ≤ 1 ppm level of oxygen and moisture for spin-casting of the photoactive layer.

The mixed solution consisting of poly(3-hexylthiophene) (P3HT) and [6,6]-Phenyl C₆₁ butyric acid methyl ester (PCBM) in 1,2-dichlorobenzene was then spin-cast at 1000 rpm on the top of the self-assembled layer of Ag nanoparticles (AgNP), as described by Li et al. [8]. The mixed solution had a P3HT:PCBM weight ratio of a 1:1 with a concentration of 20 mg/ml (P3HT). The P3HT (Merck) with 94.5% regioregularity and PCBM (Nano-C) were used without further purification. The P3HT used here has a weight-average molecular weight (M_w) of 26,200 g/mol, corre-

sponding to a number-average molecular weight (M_n) of 13,000 g/mol, and with a polydispersity (M_w/M_n) of ~ 2 .

After spin-casting the photoactive layer, thermal annealing was then performed by directly placing the device on a digitally controlled hotplate at 110 $^{\circ}\text{C}$ for 10 min in an inert glove-box. The thickness of the photoactive film was ~ 160 nm. The devices were pumped down in vacuum ($\sim 10^{-7}$ Torr) and then the multilayer stack completed by the shadowmask evaporation of a Ca (25 nm)/Al (80 nm) cathode. The final composite device structure is ITO/PEDOT:PSS/AgNP/P3HT:PCBM/Ca/Al. In our experiments, control devices (ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al) were also fabricated and tested without the self-assembled layer of Ag nanoparticles. Both sets of PV devices (control and experiment) were fabricated during the same batch processing. The active device area (A) was 0.01 cm^2 .

The current density–voltage (J – V) measurements were performed with a semiconductor characterization system (Keithley 4200) at room temperature in air without any device encapsulation under the spectral output from a 150 W solar simulator (Newport) using an AM 1.5 G filter. The solar simulator was precisely calibrated to a KG5 color filtered silicon diode (Hamamatsu S1133) as the reference cell whose spectral response matches that of the testing cells as closely as possible in order to minimize any spectral mismatching factors [33]. The irradiance (100 mW/cm^2) of the solar simulator was adjusted using a reference cell that had been recently calibrated by the National Renewable Energy Laboratory (NREL). The induced photo-current efficiency (IPCE) was measured using a current preamplifier under short-circuit conditions after illuminating the devices with monochromatic light from a quartz-halogen lamp passing through a monochromator.

3. Results and discussions

For the colloidal Ag nanoparticle in toluene with a concentration of 0.5 wt% (Metamateria Partner), an average diameter of Ag nanoparticles was ~ 3.65 nm with a very high uniformly sized distribution profile of $\sim 81\%$, determined by dynamic light scattering (Fig. 1a). The UV–vis spectrum of Ag nanoparticle solution shows a plasmon resonance peak at 412 nm with the full width at half maximum (FWHM) of ~ 61 nm, indicating the characteristics of Ag particles with a plasmon absorption band (Fig. 1b) [34].

Transmission electron microscopy (TEM) images indicate the self-assembled layer of Ag nanospheres with an average diameter of ~ 4 nm with uniform particle-to-particle spacing (Fig. 2a). In the X-ray photoelectron spectra, the Ag 3d_{5/2} peak is observed at 368.2 eV with a very narrow FWHM of 0.68 eV (not shown here), compared with elemental Ag (368.27 eV). The UV–vis spectrum of self-assembled layer of Ag nanoparticles shows the localized surface plasmon resonance peak at 465 nm with a FWHM of ~ 95 nm (Fig. 2b) [35].

Fig. 3 shows the optical density of P3HT:PCBM blend films with and without self-assembled layer of Ag nanoparticles with the red shoulder (at 602 nm), indicating effective self-organization of the regioregular P3HT [10]. In the spectral range of 350–650 nm where the P3HT:PCBM blend film is absorbing, the enhanced optical absorption was observed due to the increased electric field in the active photoactive layer by excited localized surface plasmons around the Ag nanospheres. This result corresponds to a $\sim 16\%$ increase of the total optical absorption of the devices in the spectral range of 350–650 nm.

The IPCE measurements for the control and experimental devices are shown in Fig. 4. Prior to the IPCE measurement, the spectral response of the color-filtered silicon solar cell

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