

In-situ prepared composite materials of conducting polymer-metal nanoparticles and their application to organic solar cells

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1. Introduction

Organic solar cells (OSCs) have recently been intensively studied for the next generation photovoltaic devices due to their potential to low-cost, large area, flexibility, and simple solution processability [1,2]. Although their power conversion efficiency (PCE) has been improved up to 5% based on bulk heterojunction (BHJ) of Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), further improvement up to 10% is required to successful commercialization [3,4]. The main drawback of OPV is the limitation of exciton diffusion length of about 10~20nm and poor charge transport property, thus the difficulty of increasing active layer thickness lead to insufficient absorption of incident light [5,6]. To improve light absorption in the organic photoactive layer, several methods including the introduction of new low band gap polymers [7], the use of inorganic optical spacer between active layer and metal electrode [8], and the application of surface plasmon based on metal nanoparticles (NPs) incorporated in active layer or deposited onto ITO electrode [9,10] have been reported. Among those, plasmonic enhancement is considered to be one of the best approach because of its simple process, effectiveness, and controllability of plasmon absorption wavelength by adjusting the particle size, shape, and compositions. Surface plasmons (SPs) are collective surface oscillations of conduction electrons within metal nanostructures that tend to trap optical waves near their interface between metal and dielectric medium under electromagnetic field excitation. They can create strong near-field electromagnetic fields and far-field propagating

waves, which could be used for the enhancement of light absorption and photocurrent of OSCs [11]. Three types of method using a SP phenomena of metal nanoparticle in OSCs have been reported, but they all have some drawbacks. The first is using metal nanoparticles incorporated in the photo-active layer, but in this case the PCE might be restricted by exciton quenching with nonradiative energy transfer and the differences between the electronic properties of the metal nanoparticles and the conjugated photo-active molecules [12,13]. The second is a formation of metal nanoparticle layer between ITO electrode and poly 3,4-ethylenedioxythiophene:polystyrene sulfonate (PEDOT:PSS) buffer layer, which needs one of some extra deposition process such as vacuum deposition of metal nanolayer and sequential thermal treatment, or spin coating of metal nanoparticle precursor solutions [14,15]. The third is using metal nanoparticle incorporated PEDOT:PSS layer, which needs two step of synthetic process including aqueous metal nanoparticle synthesis and their mixing with PEDOT:PSS solution[16,17].

Here we suggest more simple method to realize the surface plasmon effect by using a in-situ prepared composite materials of PEDOT:PSS-metal nanoparticle, in which Au or Ag NPs are stably incorporated.

2. Experiment

2.1 Synthesis of PEDOT:PSS-Au or Ag NPs composite materials

We have developed a novel in-situ preparation of stabilized Au or Ag NPs by reduction of chloroauric acid (HAuCl_4) or silver nitrate (AgNO_3) with sodium borohydride (NaBH_4) solution in the presence of aqueous PEDOT:PSS media. Briefly, aqueous solution of 50 mM HAuCl_4 or AgNO_3 were added into 5 ml PEDOT:PSS solution (Clevios PH500) under vigorous stirring. 100 mM of NaBH_4 was then injected into the stirred mixture very slowly (see Figure 1). AgNO_3 ($\geq 99.5\%$), HAuCl_4 ($\geq 99.9\%$), and NaBH_4 ($\geq 99\%$) were all purchased from sigma-aldrich Co., Ltd.

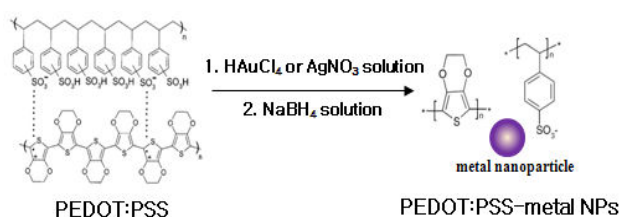


Figure 1. In-situ preparation of PEDOT:PSS-metal NPs composite solutions.

2.2. Device fabrication

In order to investigate the effect of Au or Ag NPs in PEDOT:PSS buffer layer, we made three types of OSC devices with pristine PEDOT:PSS, with PEDOT:PSS-Au NPs and with PEDOT:PSS-Ag NPs as a hole conducting buffer layer. The device configuration is glass/ITO (10~15 $\Omega/\text{sq.}$)/buffer layer (100nm)/P3HT:PCBM (100nm)/LiF (0.5 nm)/Al (150nm) as shown in Figure 2.

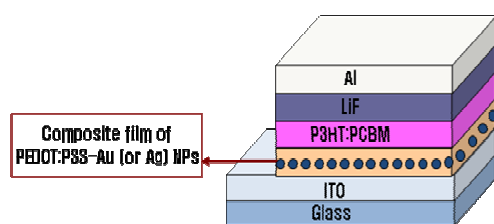


Figure 2. Structure of OSC devices.

To fabricate OSC devices, a patterned ITO glass was cleaned (treated sequentially with de-ionized water, acetone, and isopropanol in an ultrasonic bath for approximately 10 min). The buffer layer, PEDOT:PSS, was spin-coated on the ITO/glass substrate and thermally dried at 140 $^{\circ}\text{C}$ for 30 min. The photoactive layer was a mixed solution of P3HT

(Rieke Metals)/PCBM (Nano-C) blend (1:0.9) dissolved in 1,2-dichlorobenzene (DCB). The active layer was spin-coated on top of a buffer layer and dried on a hot plate for 40 min at 50 $^{\circ}\text{C}$ to give a thickness of 100 nm. Finally, cathode layer of LiF/Al was deposited by thermal evaporation under a vacuum of 1.0×10^{-7} Torr. Devices were encapsulated with cover glass to protect them from air and moisture. The post-annealing process has been done after encapsulation at 140 $^{\circ}\text{C}$ for 20 min in a N_2 filled glove box system. The active area of all of the devices was defined as 9 mm^2 by a shadow mask.

3. Results and discussion

Au and Ag NPs are one of the widely used nanomaterials in biological and electronic applications. Such applications, however, require these particles mostly to be water-dispersible and/or suspended in water without loss of physical or chemical properties over long periods of time. To obtain stable NPs in high ionic strength media (water), stabilizers such as polyvinyl-pyrrolidone (PVP), cetyltrimethylammonium bromide (CTAB), and sodium dodecylsulfate (SDS) which are hard to be removed during processing for further applications are needed. While synthetic methods of NPs in organic media were reported by several groups with well defined size and shape, they're water immiscible and have limit of application range [18]. Recently, researches on combining these NPs with PEDOT:PSS are being attempted to make hybrid materials for using as a surface plasmon source [16,17].

In our new method, we synthesize metal NPs via PEDOT:PSS media, so there is no need of using stabilizer or further mixing step of prepared metal NPs with PEDOT:PSS solution. After in-situ preparation, the color of mixed solution turned to be pale green (for Ag NPs) or medium purple (for Au NPs) from pristine royal blue (for PEDOT:PSS), indicating the Ag and Au NPs had been successfully synthesized in the PEDOT:PSS media as shown in Figure 3. The corresponding spin-coated films have also unique colors due to their surface plasmon effect.

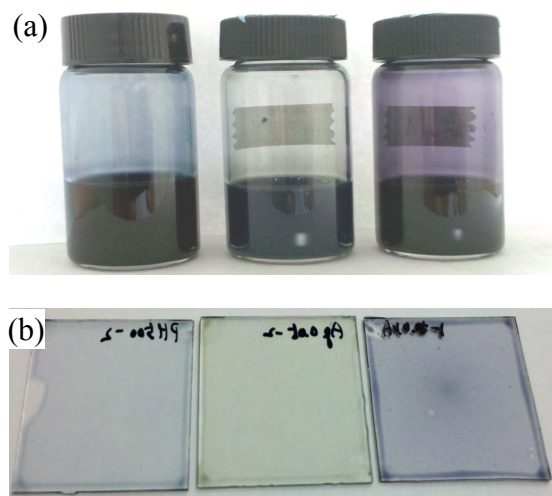


Figure 3. In-situ prepared PEDOT:PSS-metal NPs solutions (a), and its corresponding spin-coated films on the glass substrate (b). (Pristine PEDOT:PSS, PEDOT:PSS-Ag NPs, and PEDOT:PSS-Au NPs from left to right)

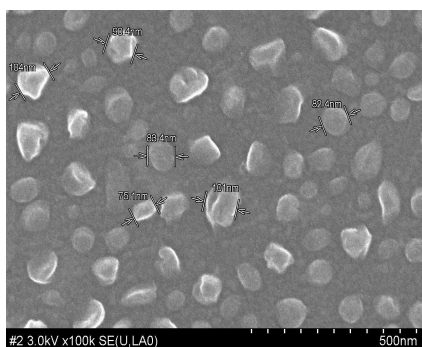


Figure 4. SEM image of Ag NPs within PEDOT:PSS media in the film state.

Figure 4 shows a scanning electron microscopy (SEM) image of synthesized Ag NPs. As we can see, Ag NPs are shapeless or roughly spherical and have average diameters of 80~100 nm with particle density of about $8 \times 10^7/\text{mm}^2$.

Ag NPs generally produce the absorption peak at 400 ~ 450 nm, and Au NPs have a surface plasmon resonance (SPR) peak between 500 and 600 nm, depending on the thickness, shape, and distance of the nanostructures [19]. Since the main absorption range of P3HT is from 400 to 650 nm, Ag and Au NPs are both appropriate materials for improving the performance of OSCs by SPR effect.

Figure 5(a) shows the absorption spectra of diluted pristine and Ag, Au NPs incorporated PEDOT:PSS solutions measured by Perkin Elmer

Lambda 750 UV/VIS spectrometer. PEDOT:PSS with Ag NPs shows a SPR peak at about 405nm, and PEDOT:PSS with Au NPs has a SPR peak at 550 nm, which are consistent with previous other reports. Figure 5(b) shows the absorption spectra of spin-coated films with glass/PEDOT:PSS-metal NPs/active layer. As we can see, the position of characteristic absorption peaks of P3HT and PCBM active layer did not much change, but its absorption intensity was significantly increased in the spectral range of 400~500 nm for Ag NPs and 500~650 nm for Au NPs.

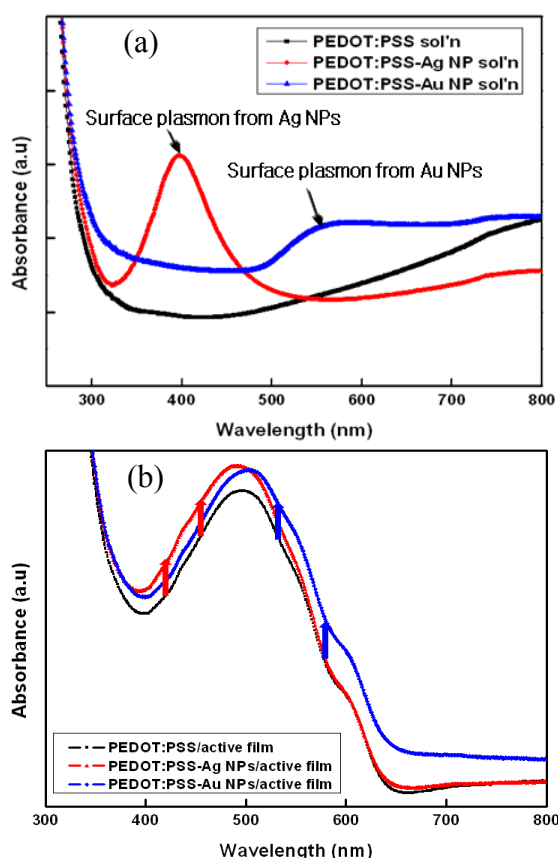


Figure 5. UV-Vis absorption spectra of the PEDOT:PSS-metal NPs in solutions (a) and in films of glass/PEDOT:PSS-metal NPs/active layer (b).

Figure 6 and table 1 show the photocurrent density-voltage ($J-V$) of three different OSC devices, measured under $100\text{mW}/\text{cm}^2$ (AM 1.5G) with a Keithley model 2400 Source-Meter and a Newport 91192 solar simulator system (equipped with 1KW xenon arc lamp, Oriel).

The reference device with pristine PEDOT:PSS buffer layer exhibited an open-circuit voltage (V_{oc}) of 0.60 V, a short-circuit current density (J_{sc}) of 6.01 mA/cm², and a fill factor (FF) of 48.6%, thus the calculated PCE was 1.74%. The PCE was improved to 1.8% by applying our synthesized PEDOT:PSS-Ag or Au NPs buffer layer. This is mainly due to enhancement of J_{sc} values, which is attributed by SPR effect as we examined in Figure 5. Although the improvement of PCE with Ag or Au NPs was not as good as we expected, we are now trying to further optimization by adjusting geometrical parameters such as the size and shape of nanoparticles.

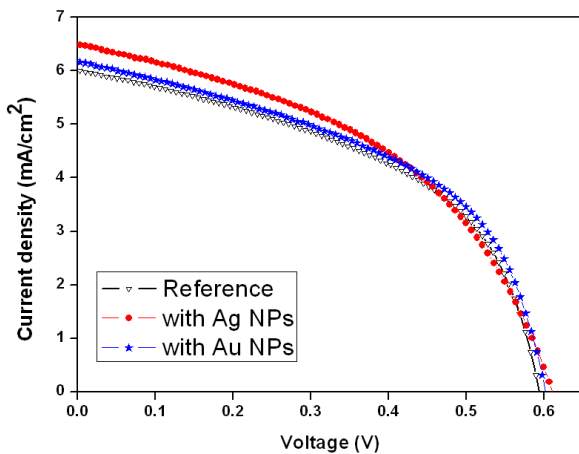


Figure 6. J - V characteristics of three devices.

Table 1. Summary of device performances.

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF(%)	PCE(%)
Reference	0.60	6.01	48.6	1.74
with Ag NPs	0.61	6.50	45.1	1.79
with Au NPs	0.60	6.17	48.5	1.80

4. Conclusions

In conclusion, we have successfully synthesized composites materials of PEDOT:PSS-Au or Ag NPs by simple in-situ preparation method. The synthesized NPs with size of 80~100nm showed well dispersed property in PEDOT:PSS media and a characteristic absorption peak due to surface plasmon resonance effect. This can enhance the light absorption ability of active layer and thus increase the efficiency of an organic solar cell. This new method is easy to synthesize and could be a suitable

solution for future practical application of organic solar cells without any change of conventional process including equipment and facilities.

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