Effect of Gold and Silver Nanoparticle in Poly(3,4-Ethylenedioxythiophene)-Poly(Styrene Sulfonate) layer on Inverted-Type Organic Thin-Film Solar Cells

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Gold- and silver-nanoparticle-incorporated inverted-type organic thin-film solar cells were fabricated and evaluated. The incorporation of gold nanoparticles, silver nanoparticles, and the gold:silver mixed nanoparticles in poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) layer, improved the photoelectric conversion efficiency of the organic thin-film solar cells under irradiation of simulated sunlight.

Key words: gold nanoparticle, silver nanoparticle, inverted-type organic thin-film solar cell

1. INTRODUCTION

Organic thin-film solar cells are attractive as the next generation of solar cells.¹, ² Typical structure of the organic thin-film solar cell is transparent electrode/hole-transport layer/photoactive layer (p-type and n-type organic semiconductors)/electrode, which are termed “normal-type”. Recently, “inverted-type” organic thin-film solar cells have attracted much interest as environmentally stable organic photovoltaics, whose structure is transparent electrode/electron-transport layer/photoactive layer/hole-transport layer/electrode.³, ⁴ Approaches from different viewpoints have been taken to achieve higher photoelectric conversion efficiencies using such solar cells.

On the other hand, plasmonic metal nanoparticles (NPs), such as those made of gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs), exhibit a localized enhanced electric field around the NP when irradiated by light, which is known as localized surface plasmon resonance (LSPR). LSPRs can excite photoactive molecules and materials. In addition, AuNPs, AgNPs, and corresponding plasmonic nanostructures seem to improve the hole-collection of conductive polymers, which has been reported.⁵⁻⁷ Therefore, plasmonic NPs such as AuNPs or AgNPs are expected to improve photoelectric conversion efficiency of organic thin-film solar cells. Many reports have verified that the incorporation of such plasmonic NPs into organic thin-film solar cells is useful for the enhancement of photovoltaic performance.⁹

The combined use of different metal NPs is also interesting. Several groups reported that a considerably stronger surface enhanced Raman scattering (SERS) signal was observed using bimetallic plasmonic materials than when a single plasmonic material was used.¹⁰⁻¹¹ From a viewpoint of photovoltaic application, we reported that the combined incorporation of AuNPs and AgNPs in hole-transport layer of the “normal-type” organic thin-film solar cell contributed to improve photoelectric conversion efficiency.¹²

While, we also reported that an enhancement of the photovoltaic performance of “inverted-type” organic thin-film solar cells was achieved by incorporation of AuNPs or AgNPs into hole-transport layer, even the NPs were placed behind the photoactive layer away from the light-facing side of the solar cell.¹³, ¹⁴ The possible reason for the enhancement of the photovoltaic performance is sum of (1) LSPR excitation of photoactive layer and (2) electric effect (such as hole-collection or conductivity change) of the incorporated NPs. Based on these backgrounds, the effect of the combined incorporation of AuNPs and AgNPs into hole-transport layer of inverted-type organic thin-film solar cells is interesting and useful to elucidate the role of plasmonic NPs in the solar cells. Therefore, in this study, inverted-type organic thin-film solar cells incorporating AuNPs, AgNPs, or AuNPs:AgNPs mixtures were fabricated and evaluated.

2. EXPERIMENTAL PROCEDURE

Regio-regular poly(3-hexylthiophene) (P3HT), [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) dispersion in water, and other chemicals were used as received.

Aqueous colloidal solutions of AuNPs and AgNPs were prepared by the reduction of HAuCl₄ and AgNO₃ with trisodium citrate salt, respectively.¹⁵ The shapes and sizes of the NPs were evaluated by transmission electron microscopy (TEM; Hitachi, H-8100). The colloidal solutions of AuNPs and AgNPs were concentrated via centrifugation.¹⁶ In the case of the AuNP or AgNP solutions, a 20 wt% of concentrated AuNPs or AgNPs solution was mixed with an aqueous solution of PEDOT:PSS, acting as the hole-transport material. In the case when a mixture of AuNPs, AgNPs,
and PEDOT:PSS was used, a 20 wt% concentrated mixed solution of AuNPs and AgNPs (AuNPs:AgNPs = 1:1) was mixed with the PEDOT:PSS solution. These solutions were denoted as PEDOT:PSS-AuNPs, PEDOT:PSS-AgNPs, and PEDOT:PSS-AuNPs:AgNPs.

The precursor solution of the titanium oxide (IV) (TiO₂) thin film that acted as the electron transport layer of the organic solar cell was prepared by mixing titanium (IV) isopropoxide (0.5 mL), 2-methoxyethanol (2.0 mL), and acetylacetone (0.5 mL). An indium-tin-oxide (ITO) transparent electrode was cleaned before use.¹⁴

The precursor solution of AuNPs or AgNPs:AgNPs solution was spin-coated on the PEDOT:PSS-AuNPs, -AgNPs or -AuNPs:AgNPs on ITO electrodes (denoted as ITO/PEDOT:PSS-AuNPs, ITO/PEDOT:PSS-AgNPs, or ITO/PEDOT:PSS-AuNPs:AgNPs).

Absorption spectra were measured by UV-Vis-NIR spectroscopy (Jasco, V-670). The current density-voltage (J-V) characteristics of the solar cells were measured using a potentiostat under illumination at 100 mW cm⁻² (AM 1.5) using a solar simulator (San-ei Electric, XES-301S).

The incident photon-to-current efficiencies (IPCE) of the solar cells were obtained from the short-circuit photocurrents under irradiation of monochromatic light (Enlitech, QE-R3011). As in both photovoltaic measurements, light was irradiated from the ITO side.

3. RESULTS AND DISCUSSION

(a) 

(b) 

TEM images of (a) AuNPs and (b) AgNPs.

The transmittance spectrum of ITO/TiO₂/P3HT:PCBM is shown in Fig. 3. Less than 10% of the irradiated light (470-540 nm) at the front of the ITO electrode reached the PEDOT:PSS layer of the solar cell. Obvious plasmonic absorption peaks of NPs were not observed. The extinction intensities of NPs in PEDOT:PSS seem to be negligibly smaller than the absorption intensity of P3HT:PCBM layer on the basis of our previous results.¹³,¹⁴

Fig. 4 shows the SEM images of ITO/PEDOT:PSS-AuNPs, -AgNPs, or -AuNPs:AgNPs. Non-uniform shaped aggregates consisting of NPs were observed in all images. The sizes of the aggregates were achieved from few to ten micrometers, which are much larger than the prepared AuNPs and AgNPs. These obvious aggregations broaden and weaken the characteristic plasmonic absorption peaks of NPs, possibly. In particular, AuNPs formed larger aggregates.
comparing with AgNPs and AuNPs:AgNPs, in PEDOT:PSS.

Fig. 5 shows the J-V characteristics of the inverted-type organic thin-film solar cells when illuminated. Each J-V curve was obtained after averaging the results of 5-6 samples.

Table 1 shows the photovoltaic performance of all analyzed solar cells. The short-circuit current densities ($J_{sc}$) of all the NP-containing solar cells are larger than that of the corresponding reference solar cell (ITO/TiO$_x$/P3HT:PCBM/PEDOT:PSS/Ag). A $J_{sc}$ enhancement ratio of up to 10% is achieved after incorporation of NPs into the solar cell. The increase of $J_{sc}$ may be due to an increased number of excitons in the P3HT:PCBM layer or a decrease of the series resistance ($R_s$) after incorporation of the NPs. Indeed, the values of $R_s$ decrease with the addition of NPs in the solar cells.

This observation is reasonable, since AuNPs and AgNPs are better conductors of electricity than PEDOT:PSS. Although, the $R_s$ values of all the NPs-containing solar cells, the $J_{sc}$ of the AuNPs-containing solar cell was smaller than the other NP-containing solar cells. This unexpected decreasing of $J_{sc}$ may be due to the difference of IPCE profiles between all the NP-containing solar cells.

On the other hand, the open-circuit voltages ($V_{oc}$) of the solar cells containing AgNPs and AuNPs:AgNPs fairly decreased when compared to that of the ITO/TiO$_x$/P3HT:PCBM/PEDOT:PSS/Ag solar cell. The reason for the decrease in $V_{oc}$ values may be the small leakage current and the work function mismatch, which is induced by the NPs into the PEDOT:PSS layers.

The power conversion efficiencies ($\eta$) of the solar cells containing NPs are larger than that of the corresponding reference solar cell. The $V_{oc}$ values and fill-factors (FFs) of the solar cells are similar for all devices. Therefore, the increase of $J_{sc}$ must be the main reason for the improvement of $\eta$ in the NP-based solar cells.

Fig. 6 shows the IPCE spectra of the inverted-type organic thin-film solar cells with and without NPs. Larger IPCE values were observed in the AgNPs- and AuNPs:AgNPs-containing solar cells than the corresponding reference solar cell in the wavelength range of 400-700 nm. In particular, the IPCE enhancement ratios of these solar cells were $> \sim$10% in the wavelength range of 470-540 nm, which are higher than the ratio of photons (less than 10%) at PEDOT:PSS.

<table>
<thead>
<tr>
<th>Solar Cell Configuration</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$R_s$ (Ω cm$^{-2}$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/TiO$_x$/P3HT:PCBM/PEDOT:PSS/Ag</td>
<td>0.53</td>
<td>5.6</td>
<td>31</td>
<td>0.46</td>
<td>1.34</td>
</tr>
<tr>
<td>ITO/TiO$_x$/P3HT:PCBM/PEDOT:PSS-AuNPs/Ag</td>
<td>0.52</td>
<td>6.0</td>
<td>23</td>
<td>0.47</td>
<td>1.48</td>
</tr>
<tr>
<td>ITO/TiO$_x$/P3HT:PCBM/PEDOT:PSS-AgNPs/Ag</td>
<td>0.51</td>
<td>6.4</td>
<td>24</td>
<td>0.45</td>
<td>1.48</td>
</tr>
<tr>
<td>ITO/TiO$_x$/P3HT:PCBM/PEDOT:PSS-AuNPs:AgNPs/Ag</td>
<td>0.51</td>
<td>6.3</td>
<td>24</td>
<td>0.46</td>
<td>1.47</td>
</tr>
</tbody>
</table>

Fig. 5 J-V characteristics of ITO/TiO$_x$/P3HT:PCBM/PEDOT:PSS-AuNPs:AgNPs/Ag (AuNPs:AgNPs), ITO/TiO$_x$/P3HT:PCBM/PEDOT:PSS-AuNPs/Ag (AuNPs), ITO/TiO$_x$/P3HT:PCBM/PEDOT:PSS-AgNPs/Ag (AgNPs), and ITO/TiO$_x$/P3HT:PCBM/PEDOT:PSS/Ag (without NPs).

Table 1. Photovoltaic performances of solar cells.
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4. CONCLUSIONS

We demonstrated the fabrication and evaluation of inverted-type organic thin-film solar cells incorporating AuNPs, AgNPs, and a AuNPs:AgNPs mixture in the hole-transport layer of solar cell. Enhancement of photoelectric conversion efficiency was achieved by incorporation of gold and silver NPs, even the NPs were placed at the dark side of the solar cell. Mixing effect of gold and silver NPs for improvement of photovoltaic performances was not observed.

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