Research Article

Effects of Au Nanoparticle Addition to Hole Transfer Layer in Organic Photovoltaic Cells Based on Phthalocyanaines and Fullerene

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Phthalocyanaines/fullerene organic photovoltaic cells were fabricated and characterized. Effects of Au nanoparticle addition to a hole transfer layer were also investigated, and power conversion efficiencies of the photovoltaic cells were improved after blending the Au nanoparticle into PEDOT:PSS. Nanostructures of the Au nanoparticles were investigated by transmission electron microscopy and X-ray diffraction. Energy levels of molecules were calculated by molecular orbital calculations, and the nanostructures and electronic property were discussed.

1. Introduction

In noble metal particles such as gold or silver from tens of nanometer to several nanometers, the vibrational frequency of localized surface plasmon resonates with a photoelectric field of the wavelength of the visible region [1–4]. When visible light is irradiated to noble metal nanoparticles or nanostructures, light is converted into surface plasmon and the localized electric field generated in the vicinity of surface of nanoparticles or nanostructures. The plasmon electric field is excited dye molecules as well as light, and interesting phenomena and various applications have been reported [5–8]. In addition, the group velocity of light decreases in such nanospace and the photoabsorption efficiency of dye arranged in the nanospace would be reinforced. Therefore, clarifications and applications of the reinforcement mechanism are interesting research objects.

Phthalocyanaines have been widely studied as attractive materials for photovoltaic, electrochemical, gas-sensing, and data-storage devices [9, 10]. Phthalocyanaine molecules have planar unit and electronic conductivity because of the π electron system and have p-type semiconductor behavior [11]. Therefore, they have been investigated as thin film organic photovoltaic cells, which are expected as next-generation photovoltaic cells because of advantages of easy manufacture process, low production cost, and flexibility [12–14]. The photovoltaic devices consisting of noble metal nanostructures or nanoparticles with the localized electric field have been reported [15, 16]. However, there are few studies on organic photovoltaic cells with noble metal nanostructures or nanoparticles.

The purpose of the present work is to fabricate and characterize organic photovoltaic cells based on phthalocyanaines and fullerene (C60). In the present work, C60 was used as n-type semiconductor, and copper naphthalocyanine (CuNc) and subphthalocyanine (SubPc) were used as p-type semiconductors, respectively. In addition, effects of Au nanoparticle (AuNP) addition to a hole transfer layer were investigated. For metal nanoparticles such as Au and Ag, strongly enhanced electric fields are locally generated in their nanospaces by irradiation of light. This phenomenon is due to localized surface plasmon resonance (LSPR), which is
expected to enhance light harvesting of the organic solar cells [15–19]. Photovoltaic devices were fabricated, and nanostructures, electronic property, and optical absorption were investigated.

### 2. Experimental Procedures

Aqueous stock solution of HAuCl₄ (2.5 × 10⁻⁴ M) was prepared and refluxed. After reflux for 40 min, 1 wt.% sodium citrate of 1.4 mL was added to reaction mixture. After reflux for 60 min, it was cooled under the air atmosphere. The fabricated AuNP solution was concentrated by the centrifugation. To prepare the composite buffer layer, the concentrated AuNP solution was blended into the polyethyleneoxythiophene doped with polystyrene sulfonic acid (PEDOT:PSS, Sigma-Aldrich Corp.) solution. The volume ratio of AuNP solution was 20%.

A buffer layer of PEDOT:PSS with AuNPs was spin coated on precleaned indium tin oxide (ITO) glass plates (Geomatec Co. Ltd., ∼10 Ω cm⁻²). After annealing at 100 °C for 10 min in N₂ atmosphere, p-type photoactive layers were prepared on a PEDOT layer. Copper (II) 2,3-naphthalocyanine (CuNc, Sigma-Aldrich Corp., 85%) layers were deposited by a spin coating method, and subphthalocyanine (SubPc, Orient Chemical Industries Co., Ltd.) layers were deposited by evaporation, respectively. After depositing p-type photoactive layers, C₆₀ thin films were deposited using C₆₀ powder (Material Technologies Research Ltd., 99.98%) by a vacuum deposition method. Aluminum (Al) metal contacts with a thickness of 100 nm were evaporated as a top electrode. A schematic diagram of the present photovoltaic cells is shown in Figure 1.

The current density-voltage (J–V) characteristics (Hokuto Denko Co. Ltd., HSV-110) of the photovoltaic cells were measured both in the dark and under illumination at 100 mW cm⁻² by using an AM 1.5 solar simulator (San-ei Electric Co. Ltd., XES-301S). The photovoltaic cells were illuminated through the side of the ITO substrates, and the illuminated area is 0.16 cm². Incident photon to current conversion efficiency (IPCE) was measured by using hypermonolight (Bunkoukeiki Co. Ltd., SM-25) and potentiostat (Huso Ltd., HECS 318C). The photovoltaic cells were irradiated by monochromated Xe lamp from the ITO side. Absorption spectra were measured by means of UV-visible spectroscopy (JASCO, V-670), and the wavelength region is in the range of 300 nm to 400 nm. Microstructures of AuNPs were analyzed using X-ray diffractometer (Philips X’ Pert-MPD System) with CuKa radiation operating at 40 kV and 40 mA. Transmission electron microscope (TEM) observation was carried out by a 200 kV TEM (Hitachi, H-8100).

The isolated molecular structures were optimized by ab initio molecular orbital calculations using Gaussian 03. Conditions in the present calculation were as follows: calculation type (SP), calculation method (B3LYP), and basis set (LANL2DZ). Electronic structures such as energy gaps between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), and electron densities were investigated.

### 3. Results and Discussion

A TEM image and an electron diffraction pattern of AuNP are shown in Figures 2(a) and 2(b), respectively. AuNPs have an fcc structure with a lattice parameter of a = 0.40786 nm. In the TEM image of Figure 2(a), AuNPs have a spherical shape and grain sizes of AuNPs were in the range of 40–60 nm. An X-ray diffraction pattern of the AuNPs sample prepared by the present reduction method is shown in Figure 3. From a 111 diffraction peak, a grain size was calculated by using Debye-Scherrer formula: D = 0.9λ/βcosθ, where λ, β, and θ represent the wavelength of X-ray source, the full width at half maximum (FWHM), and the Bragg angle, respectively. An average particle size is calculated to be 42 nm, which agrees well with the observed TEM data as shown in Figure 2(a).

Figure 4 shows absorption spectra of AuNP solution and AuNPs in PEDOT:PSS deposited by a spin coating method on glass substrates. In Figure 4, absorption peaks were confirmed to be 536 and 578 nm, respectively, which were originated from plasmon absorption.

Optical absorption spectra of CuNc/C₆₀ and SubPc/C₆₀ thin film on glass substrate are shown in Figures 5(a) and 5(b), respectively. In Figure 5(a), absorption peaks at 350 nm and 450 nm are due to C₆₀ and other peaks are due to CuNc. In Figure 5(b), an absorption peak at 580 nm is due to SubPc. The present CuNc/C₆₀ and SubPc/C₆₀ heterojunction structures with AuNPs provided absorbance increase for the wavelength from 500 nm to 700 nm.

Measured J–V characteristics of CuNc/C₆₀ and SubPc/C₆₀ photovoltaic cells with or without AuNP under illumination are shown in Figure 6. The present structures show characteristic curve for open-circuit voltage and short-circuit current. Measured parameters of the present photovoltaic cells are summarized in Table 1. In Table 1, CuNc/C₆₀ and SubPc/C₆₀ heterojunction structures with AuNPs provided higher short-circuit current compared to those of CuNc/C₆₀ and SubPc/C₆₀ structures without AuNP. The SubPc/C₆₀
heterojunction structure with AuNPs provided short-circuit current ($J_{sc}$) of 0.44 mA cm$^{-2}$, open-circuit voltage ($V_{oc}$) of 0.55 V, fill factor (FF) of 0.28, and power conversion efficiency ($\eta$) of 0.068%, respectively.

Figure 7 shows the incident photon to current conversion efficiency (IPCE) spectra of SubPc/C$_{60}$ photovoltaic cells with or without AuNP. The photovoltaic cells with AuNPs demonstrated the high IPCE spectrum in the range of 500–600 nm, which corresponded well with the absorption peak of AuNPs as observed in Figure 4.

Electronic structures, HOMOs, LUMOs, and energy gaps of CuNc and SubPc are shown in Figure 8. HOMO and LUMO of CuNc were calculated to be $-3.13$ eV and $-5.01$ eV, respectively, on the basis of molecular orbital calculation. HOMO and LUMO of SubPc were calculated to be $-3.02$ eV and $-5.74$ eV, respectively.

An energy level diagram of the present photovoltaic cells is summarized as shown in Figure 9. Previously reported values were also used for the energy levels [20–22]. The carrier transport mechanism is considered as follows. When light is incident from the ITO substrate, light-absorption excitation occurs at the Pcs/C$_{60}$ interface and electrons and holes are produced by charge separation. Then, the electrons transport through C$_{60}$ toward the Al electrode, and the holes transport through PEDOT:PSS to the ITO substrate. Since it has been reported that $V_{oc}$ is nearly proportional to the difference between HOMO of electronic donor (Pcs) and LUMO of electronic acceptor (C$_{60}$) [23], the difference of $V_{oc}$ would be considered to be the combination of Pcs and C$_{60}$.

In the present work, organic photovoltaic cells with AuNPs based on phthalocyanines and C$_{60}$ were fabricated and characterized. Performance of the present photovoltaic
Table 1: Experimental parameters of the present photovoltaic cells.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>$V_{oc}$/V</th>
<th>FF</th>
<th>$\eta$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuNc</td>
<td>0.012</td>
<td>0.13</td>
<td>0.25</td>
<td>$3.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>CuNc (AuNP)</td>
<td>0.034</td>
<td>0.12</td>
<td>0.24</td>
<td>$9.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>SubPc</td>
<td>0.39</td>
<td>0.55</td>
<td>0.27</td>
<td>0.058</td>
</tr>
<tr>
<td>SubPc (AuNP)</td>
<td>0.44</td>
<td>0.55</td>
<td>0.28</td>
<td>0.068</td>
</tr>
</tbody>
</table>

4. Conclusions

Organic photovoltaic cells were fabricated by using C$_{60}$ as n-type semiconductor, and CuNc and SubPc as p-type semiconductors, respectively. $J$-$V$ characteristics were investigated under illumination to confirm the photovoltaic cell performance. CuNc/C$_{60}$ heterojunction structure with AuNPs provided photoabsorption in the range of 500 to 700 nm and provided $\eta$ of $9.8 \times 10^{-4}$%, FF of 0.24, $J_{sc}$ of 0.034 mA cm$^{-2}$, and $V_{oc}$ of 0.12 V. The device was based on the SubPc/C$_{60}$ heterojunction structure with AuNPs provided $\eta$ of 0.068%, FF of 0.28, $J_{sc}$ of 0.44 mA cm$^{-2}$, and $V_{oc}$ of 0.55 V. Nanostructures of AuNPs were investigated further.
by TEM and X-ray diffraction, and the grain sizes of the AuNPs were determined to be 40–60 nm. Energy levels of the molecules were calculated by molecular orbital calculations.

**References**


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