

# **POLY(3,4-ETHYLENEDIOXYTHIOPHENE) : POLY(STYRENESULFONATE) / SINGLE-WALL CARBON NANOTUBE COMPOSITE FILM FOR THE HOLE TRANSPORT LAYER IN POLYMER SOLAR CELLS**

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The Composite thin film of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)/single-wall carbon nanotubes (PEDOT:PSS/SWCNTs) for a hole transport layer in polymer solar cells have been explored. By loading 0.5 wt% of SWCNTs, PEDOT:PSS/SWCNT composite film exhibited higher electrical conductivity than the control PEDOT:PSS film, suggesting the increase in carrier transport passes through SWCNTs in the hole transport layer. We also demonstrated the improvement of a fill factor and short circuit current density in the polymer solar cells with the hole transport layer of PEDOT:PSS/SWCNT as compared with PEDOT:PSS.

Keywords; Single-wall carbon nanotubes; Polymer nanocomposite film; Polymer solar cells

## **1. Introduction**

Polymer solar cells have attracted much attention in recent years for their potential for flexible, light weight and low cost application to solar energy conversion. Since the development of bulk heterojunction concept for solution processed polymer solar cells<sup>1-3</sup>, a lot of efforts have been dedicated to the improvement of power conversion efficiency (PCE) by using new organic materials for photovoltaic<sup>4,5</sup> and hole transport layers<sup>6,7</sup>. Recently, Liang *et al.* reported that the PCE of polymer solar cells reaches around 7%

by using a benzodithiophene based polymer/phenyl-C71-butyric acid methyl ester system as the photovoltaic layer<sup>5</sup>.

A hole transport layer, which is formed between the hole correcting anode and the photovoltaic layer in the polymer solar cell, plays an important role on the control of the hole injection to the anode. Several kinds of conducting polymers<sup>6,7</sup> have been investigated as materials for the hole transport layer of polymer solar cells. In particular, it has been reported that the hole transport layer of poly(3,4-

ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) improves the hole collection and increases the open circuit voltage ( $V_{oc}$ ) in polymer solar cells<sup>8</sup>. On the other hand, insertion of PEDOT:PSS reduces the fill factor (FF) and short circuit current density ( $J_{sc}$ ) owing to the increased series resistance ( $R_s$ ) of the devices<sup>9</sup>. Therefore the electrical conductivity of PEDOT:PSS layer is considerably important for the better device performance of polymer solar cells. Ko *et al.* demonstrated that the high conducting PEDOT:PSS doped with mannitol results in the reduction of  $R_s$  that contributes to improve PCE of the polymer solar cells<sup>10</sup>. Improving efficiency of multi-layered organic solar cells using PEDOT:PSS blended with functionalized multi-wall carbon nanotubes as a hole transport layer has recently been reported<sup>11</sup>, although the device performance is still insufficient for the practical use. Thus, further studies on high conductive materials for the hole transport layer are required to develop polymer photovoltaic devices with high PCE.

Single-wall carbon nanotubes (SWCNTs) have attracted as a novel electric material due to their unique electronic property originated from quasi one dimensional structure<sup>12</sup>. With an aim to improve the performance of the organic solar cells, SWCNTs have been incorporated into the devices. Kymakis *et al.* reported that fullerene derivatives, which work as an acceptor material in the photovoltaic layer, can be replaced with SWCNTs<sup>13</sup>. SWCNTs have also emerged and investigated as a conductive filler for composite materials<sup>14</sup>. Their small size, large aspect ratio, and high conductivity make it possible to create the highly conductive composite with low filling concentrations. Conductivity of PEDOT:PSS has been improved by adding small amount of functionalized SWCNTs<sup>15</sup>. A transparent conductive film of PEDOT:PSS blended with SWCNTs has recently been demonstrated as a substitute of indium tin oxide (ITO), which acts as the anode electrode in organic solar cells<sup>16</sup>.

In this work, we report the exploration of PEDOT:PSS/SWCNTs as a material for the hole transport layer of polymer solar cells. The electrical conductivity of PEDOT:PSS/SWCNT film was enhanced as compared with that of PEDOT:PSS because of the carrier transport pass through SWCNTs.

Moreover, we have fabricated polymer solar cells with the hole transport layer of PEDOT:PSS/SWCNTs to investigate the significance of SWCNTs incorporation into the hole transport layer on the device performance.

## 2. Experimental details

PEDOT:PSS/SWCNT composite films were prepared by the spin casting method as follows: PEDOT:PSS solution (conductive grade) was purchased from Sigma-Aldrich. SWCNTs synthesized by eDIPS method<sup>17</sup> were dispersed in sodium dodecyl sulfate (SDS) 1wt% aqueous solution by ultrasonication for 10min. Dispersions were centrifuged at 3000 rpm for 1 day. Mixed dispersions of PEDOT:PSS and SWCNTs with the ratio of 3:1 in volume were spin cast on quartz substrates for the film formation. The ratio of SWCNTs to PEDOT:PSS in the composite film was controlled by the concentration of SWCNTs in the dispersion. For the comparison study, the control PEDOT:PSS film was formed similarly by using PEDOT:PSS solution diluted with SDS 1wt% aqueous solution with ratio of 3:1 in volume. After spin casting, films were annealed at 100 °C for 5 min to evaporate water. Film thicknesses measured by using a surface profiler (ULVAC Veeco, Dektak 150) were around 50 nm. Sheet resistances of films were measured by four point probe technique at room temperature. Electrical conductivities of films were calculated by measured sheet resistances and the film thickness of 50 nm. Transmission spectra and surface morphologies of films were characterized by using a spectrophotometer (JASCO V-570) and an atomic force microscopy (AFM, Seiko Instruments SPI3700/SPA300), respectively.

Polymer solar cells with the hole transport layer of PEDOT:PSS/SWCNT composite were fabricated on ITO coated glass substrates. The composite hole transport layer was formed on ITO by spin coating of the mixture dispersion of PEDOT:PSS and SWCNTs, followed by annealing at 100 °C for 5 min. The control polymer solar cell was also fabricated similarly by using PEDOT:PSS solution, which is diluted with SDS aqueous solution to be the same concentration as that with SWCNTs. As a photovoltaic layer of polymer solar cells, blends of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) (1:1 in weight) were spin-coated from

dichlorobenzene solution onto the hole transport layer. After spin casting, device samples were thermally annealed at 100 °C for 30 min to evaporate the organic solvent. Aluminum (Al) was used as a top electrode. The device area is 0.09 cm<sup>2</sup>. Current density–voltage (*J*-*V*) characteristics of polymer solar cells were measured in dark and under illumination at 100 mW/cm<sup>2</sup> by using an AM 1.5 solar simulator.

### 3. Results and discussion

Fig. 1(a) shows the electrical conductivity of PEDOT:PSS/SWCNT composite film plotted against SWCNT loading, i.e. SWCNTs/(SWCNTs+PEDOT:PSS) that can be calculated using weights of SWCNTs and PEDOT:PSS in the aqueous dispersion. The conductivity of the composite film monotonically increases with an increase in the SWCNT loading and, therefore, the amount of incorporated SWCNTs. In contrast to the average conductivity of 190 S/m in the control PEDOT:PSS film, that of the composite film increases up to 310 S/m at the SWCNT loading of 0.5 wt%. This conductivity enhancement results from carrier transport through the incorporated SWCNTs, which have higher carrier mobilities than PEDOT:PSS.

For the use of the hole transport layer with enhanced conductivity in the polymer solar cells depicted in Fig. 2, the composite film of PEDOT:PSS/SWCNTs should need to be enough transparent because solar light reaches to the photovoltaic layer through the hole transport layer. In order to characterize the transparent property of PEDOT:PSS/SWCNT film, the optical transmission spectra of the composite film including ITO/glass substrates were measured. As shown in Fig. 1(b), while the transmission of the control PEDOT:PSS film on ITO/glass was 84.4 % at 550 nm, that of the

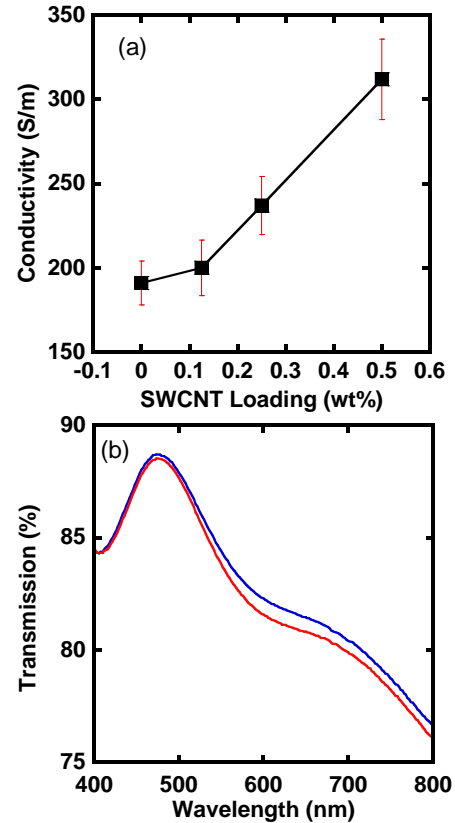


Fig. 1 (a) A plot of the electrical conductivities of PEDOT:PSS/SWCNT films against SWCNT concentrations in the composite. All composite films were fabricated on quartz substrates. (b) Optical transmission spectra of thin films of PEDOT:PSS (blue) and PEDOT:PSS including 0.5wt% of SWCNT (red) formed on ITO/glass substrates.

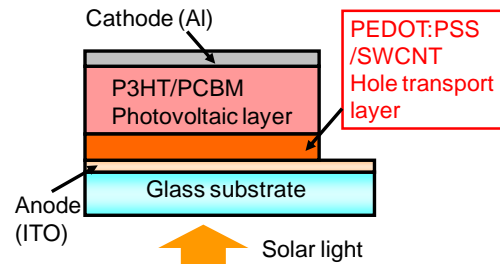


Fig. 2 Schematic depiction of P3HT/PCBM based solar cell with PEDOT:PSS/SWCNT composite hole transport layer.

Table 1. Device performances of polymer solar cells with PEDOT:PSS and PEDOT:PSS/SWCNT composite films as the hole transport layer. Concentration of SWCNTs in the composite hole transport layer is 0.25 wt%.  $R_s$  and  $R_{sh}$  are obtained by the curve-fitting of *J*-*V* curves measured under dark condition.

Hole transport layer of solar cells	PCE (%)	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF (%)	$R_s$ (Ωcm <sup>2</sup> )	$R_{sh}$ (Ωcm <sup>2</sup> )
PEDOT:PSS	1.94	6.68	0.61	47.7	4.5	$9.0 \times 10^6$
PEDOT:PSS/SWCNTs	2.12	6.91	0.59	51.7	2.7	$1.2 \times 10^3$

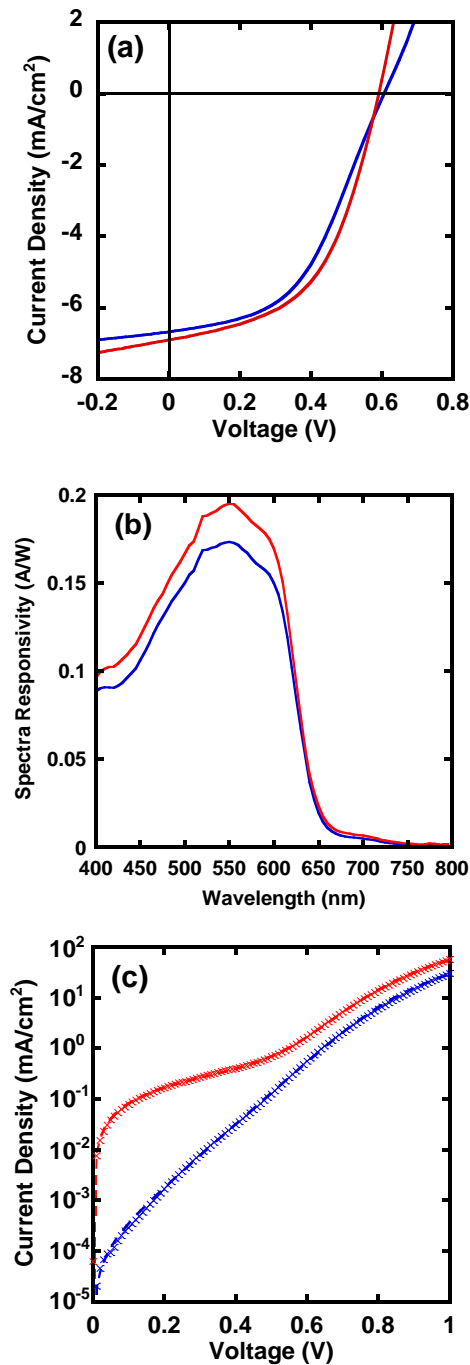


Fig. 3 (a)  $J$ - $V$  plots under illumination for polymer solar cells with PEDOT:PSS (blue) and PEDOT:PSS/SWCNT composite (red) as the hole transport layer. Concentration of SWCNTs in the composite hole transport layer is 0.25 wt%. (b) Spectral response for devices with PEDOT:PSS (blue) and PEDOT:PSS/SWCNT composite (red) as the hole transport layer. (c)  $J$ - $V$  plots for polymer solar cells with PEDOT:PSS (blue-cross) and PEDOT:PSS/SWCNT composite (red-cross) as the hole transport layer measured under dark condition. Dashed lines indicate the fitted curve of  $J$ - $V$  plots.

composite sample with 0.5 wt% of SWCNTs was

observed to be 83.9 %. Therefore, it was concluded that the incorporation of SWCNTs does not affect on the transmission of the hole transport layer so much at the SWCNT loading of less than 0.5 wt%.

Fig. 3 (a) shows  $J$ - $V$  characteristic under illumination for the polymer solar cells with the PEDOT:PSS and PEDOT:PSS/SWCNT composite films as a hole transport layer. Table 1 summarizes the device performance of solar cells, that clearly shows considerable improvements of FF and  $J_{sc}$  in the solar cells with the composite hole transport layer as compared with that of the control device. These improvements contribute to enhance PCE of solar cells from 1.94% to 2.12%. Fig. 3 (b) shows the spectral response of the fabricated devices. The improvement in  $J_{sc}$  agrees with the spectral response curves.  $R_s$  and shunt resistance ( $R_{sh}$ ) of the solar cells were estimated by curve-fitting<sup>18</sup> of the  $J$ - $V$  curves measured under dark condition as shown in Fig. 3 (c). It was found that  $R_s$  is improved by adding SWCNTs into the hole transport layer from 4.5  $\Omega\text{cm}^2$  to 2.7  $\Omega\text{cm}^2$ . This improvement would be the main reason for increases in PCE in the solar cell with the composite hole transport layer. For further improvement of PCE, we fabricated devices with post annealing at 140  $^\circ\text{C}$  for 10 min in  $\text{N}_2$  ambient after deposition of Al electrode<sup>19</sup>. We confirmed that incorporation of SWCNTs into the hole transport layer is also effective to the device with the post annealing process. The post annealed solar cells with PEDOT:PSS and PEDOT:PSS including 0.25wt% of SWCNTs show PCE of 2.19% and 2.68%, respectively.

Although the control device shows the high  $R_{sh}$ <sup>20</sup>, reduction of  $R_{sh}$  was confirmed in the device with the composite hole transport layer as shown in Table 1. To investigate the origin of the  $R_{sh}$  reduction, we have characterized the surface morphology of the composite hole transport layer. Figs. 4 show typical AFM images of the PEDOT:PSS and PEDOT:PSS/SWCNT composite films formed on glass substrates. While the control PEDOT:PSS film has a relatively smooth surface (Fig. 4(a)), SWCNTs bundles are clearly observed on the surface of the composite film (Fig. 4(b)). Therefore, in the solar cell with the composite hole transport layer, it is suggested that exposed SWCNT bundles invade into the photovoltaic layer and directly bridge between the anode electrode and

the photovoltaic layer. Because SWCNT samples used in this study contain both semiconducting and metallic SWCNTs, exposed metallic SWCNTs on the surface of the hole transport layer behave as recombination centers<sup>13</sup> and the leakage pass of photogenerated electrons into the anode electrode. These behaviors can induce the current leakage as confirmed in the  $J$ - $V$  curve of the device with the composite hole transport layer in Fig. 3(a). Current leakage increases with increasing concentration of SWCNTs in the composite hole transport layer. Therefore, excess incorporation of SWCNTs decreases device performance. The solar cell with 0.5wt% of SWCNTs exhibits large leakage

$V_{oc}$  of the solar cell with the composite hole transport layer<sup>21</sup>.

#### 4. Summary

The conductivity enhancement in PEDOT:PSS based film by adding SWCNTs and the application for the hole transport layer in polymer solar cells have been reported. Insertion of PEDOT:PSS/SWCNT layer resulted in the improvement of  $J_{sc}$  and FF because of the reduction of the series resistance. However, simultaneously the incorporation of SWCNTs increased the leakage current of the device, probably due to SWCNTs protruding from the hole transport layer. Further studies on optimizing the device structures are required for reducing the leakage current, which should lead to the more improvement of PCE in polymer solar cells with polymer/SWCNT composites.

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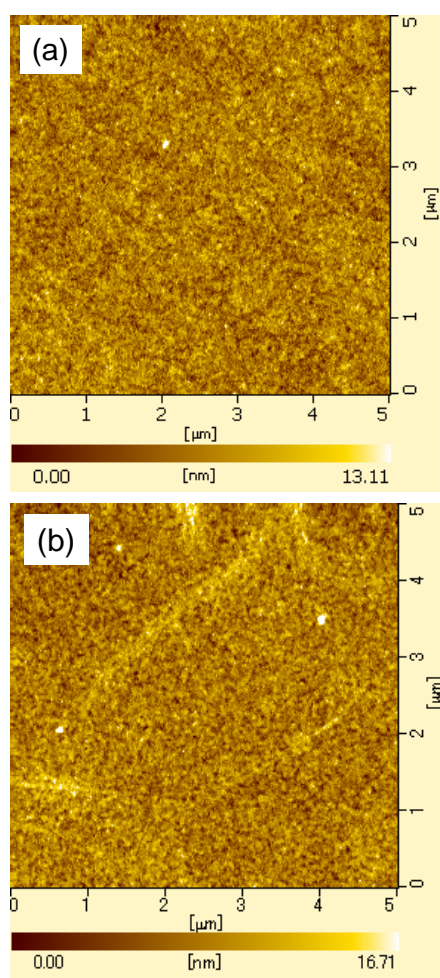


Fig. 4 AFM images of (a) PEDOT:PSS and (b) PEDOT:PSS/SWCNTs composite films formed on glass substrates. Concentration of SWCNTs of the composite film is 0.25wt%. SWCNT bundles are observed on the surface of PEDOT:PSS/SWCNT composite film.

current and PCE of 1.55%. This scenario of the leakage current induced by exposed SWCNTs is also consistent with the observation of slight decreasing in

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