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ORIGINAL ARTICLE - NANOMATERIALS

CNT/AgNW Multilayer Electrodes on Flexible Organic Solar Cells

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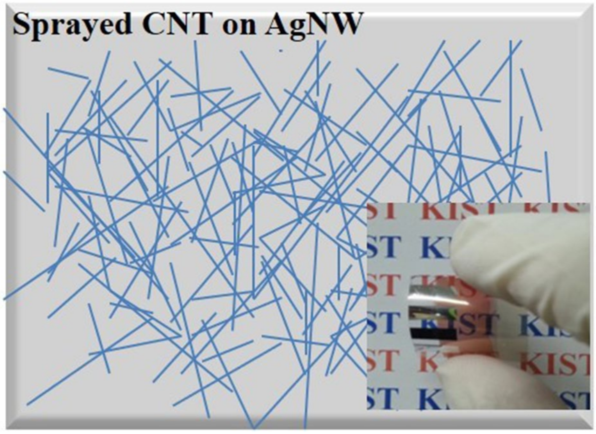
Abstract

In this study, the fabrication of transparent CNT/AgNW multilayer electrodes on PET substrates using a spray coating process is investigated. A CNT/AgNW multilayer electrode exhibited a R_{sh} of 50 Ω/square with a transparency of 94% at 500 ~ 550nm wavelength without substrate. We examined the effects of the sheet resistance and transparency of CNT/AgNW multilayer electrodes based on the performance of the OSC cells. The use of sprayed CNT/AgNW multilayer electrodes will advance the mass production of inexpensive and highly efficient flexible polymer organic solar-cell based films using a roll-to-roll based process.

Graphic Abstract



Keywords CNT · AgNW · PET · Solar cell · ITO · Ta

1 Introduction

The flexible transparent electrode applies smart windows, organic solar cells (OSC), and organic light emitting diodes (OLED) to flexible electronic devices. Transparent and flexible electrode, ITO (indium-tin oxide) can be used in photovoltaic solar cells as a substitute for conductive oxide. However, ITO films are deposited using relatively slow vacuum-based processes, and indium materials are expensive materials. Therefore, considerable efforts have been made for the development of flexible transparent electrodes comprising carbon nanotubes (CNT), graphene, silver nanowires (AgNW) and metal grids.

The transparent and conductive CNT [1–5] electrodes are rich in feedstock and coating processes, which can significantly reduce costs. Different study groups reported that co-functionalized CNTs could be used to prepare thin films with improved transport properties, and generally

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reported transparency of approximately 85% for a sheet resistance(R_{sh}) of ~ 100 Ω/square. However, the sheet resistance of CNT transparent electrodes is too high for use in organic solar cells, which requires low sheet resistance (10 Ω/square) and high transparency (~ 85%). Therefore, a substantial improvement in sheet resistance of the CNT film is needed. Among these materials, AgNW shows excellent electrical conductivity due to the low resistivity of silver. In addition, AgNW is cost-effective due to its large surface area and solution processability [6]. A breakthrough in this area is that CNT/AgNW multilayer materials are much better than using CNT and AgNW separately [7–9]. Zhu et al. [10] reported that the performance of graphene / metal grid hybrid electrodes is better than the corresponding single component transparent conductive electrodes. In Kyu Moon et al. [11] reported that graphene oxide as an overcoat layer and protective layer of AgNW conductive nanowire electrodes applied using the spray method achieves a film with strong substrate adhesion, high mechanical stability, and reduced and uniform sheet resistance. At that time, R_{sh} is 25 Ω/square and transmittance is 92% at 500 ~ 550 nm wavelenth, respectively. Many groups have announced high-performance transparent film heaters based on hybrids of CNT and AgNW, but the effect of sheet resistance and transparency of AgNW-based multilayer electrodes on the performance of OSC has yet to be studied [12, 13].

In this study, the fabrication of transparent CNT/AgNW multilayer electrodes on polyethylene terephthalate (PET) substrates using a spray coating process was investigated, and changes in the electrical and optical conductivity of the electrodes were discussed. We also examined the effects of the sheet resistance and transparency of the electrodes based on the performance of OSC cells.

2 Experimental Procedure

With an average diameter and length of approximately 45 nm and 40 µm, respectively, AgNWs were synthesized using a modified polyol process. A clean flask was placed in a heating mantle. A mixture of 0.334 g of poly vinylpyrrolidone (PVP) and 20 mL of ethylene glycol (EG) was heated in a clean flask at 170 °C for 2.5 hours to remove any remaining moisture in the PVP. In addition, 0.025 g of silver chloride (AgCl) was finely ground and added to the flask for initial nucleation of the silver seeds. Using 0.110 g of silver nitrate ($AgNO_3$), the actual silver source was titrated for 20 min. The flask was then heated for an additional 30 minutes to ensure complete growth. Finally, the washed AgNWs were stored in methanol and dispersed in isopropyl alcohol. The arc-discharge single wall CNT(SWCNT) powder applied was purchased from NANO Solution Co., Ltd. The length is typically 5–20 µm with a diameter of 1.2–1.8 nm. CNTs with a purity of approximately 30 at.% were fabricated. The surfaces of the SWCNTs were functionalized using sodium dodecyl sulfate (SDS, CH_3, $(CH)_{211}$ OSO_3 Na) with a deionized water base. SWCNTs of 0.03 wt.% and 0.2 wt.% in an aqueous solution of SDS were mixed and sonicated for approximately 1 hour to disperse the CNTs. The surfactant SDS molecules were adsorbed into the surface of the CNTs, forming a monolayer allowing the CNTs to be uniformly dispersed.

AgNW and CNT/AgNW multilayer network films were coated with a barrier/PET film using a spray coating method. For one cycle of spraying, 0.5 mL of a dispersed solution was used at room temperature in air and under an N_2 atmosphere of 0.02 MPa. During the spraying process, the substrate holder was kept at 100 °C to accelerate evaporation of the fine droplets on the surface. An increase in the spray cycles led to thicker films. When the spray process was terminated, the CNT film was immersed into deionized water for 1 minute to remove the SDS surfactant, and then blow-dried in N_2 at a temperature of 100 °C for 10 minutes. In these experiments, it was found that spray coating results in a microscopically homogeneous film with a surface area of 500 cm^2. The sheet resistance and optical transmission properties of the flexible transparent electrodes were measured using a four-point probe method (Keithley 2001 multimeter) and UV–visible spectrometer (Lambda 18), respectively. A scanning electron microscope (SEM, FEI XL-30 FEG) was used to analyze the morphology of the flexible transparent films. The surface morphology was examined using atomic force microscopy (AFM, VEECO D 3100).

We fabricated a conventional bulk hetero-junction polymer solar cell on AgNW/brrier/PET, CNT/AgNW/barrier/PET, and reference ITO/Glass. A PEDOT:PSS (Clevios PH1000, purchased from H.C. Starck) layer was spin-coated onto electrode substrates at 4000 rpm for 40 seconds, and annealed on a hot plate at 130 °C for 30 minutes inside a glove box. Next, to make an organic solar cells, a blend solution of P3HT/PCBM in a 1:0.8 weight ratio in chlorobenzene was spin-coated onto the PEDOT:PSS layer at 2500 rpm for 40 seconds. P3HT/PCBM devices were annealed on a hot plate at 150 °C for 10 minutes inside a glove box. Finally, a reflective metal cathode consisting of 100-nm Al on top of 0.8-nm LiF was thermally evaporated through a shadow mask to produce an active area of 9 mm^2 under a high vacuum pressure. To investigate the current–voltage (I-V) curves of solar cells, a Keithley 2400 multimeter instrument was used. All photovoltaic devices were measured in air at room temperature and under AM 1.5G illumination conditions of 100 $mWcm^{-2}$. For an accurate measurement, the light intensity was calibrated using a standard Si photovoltaic cell.

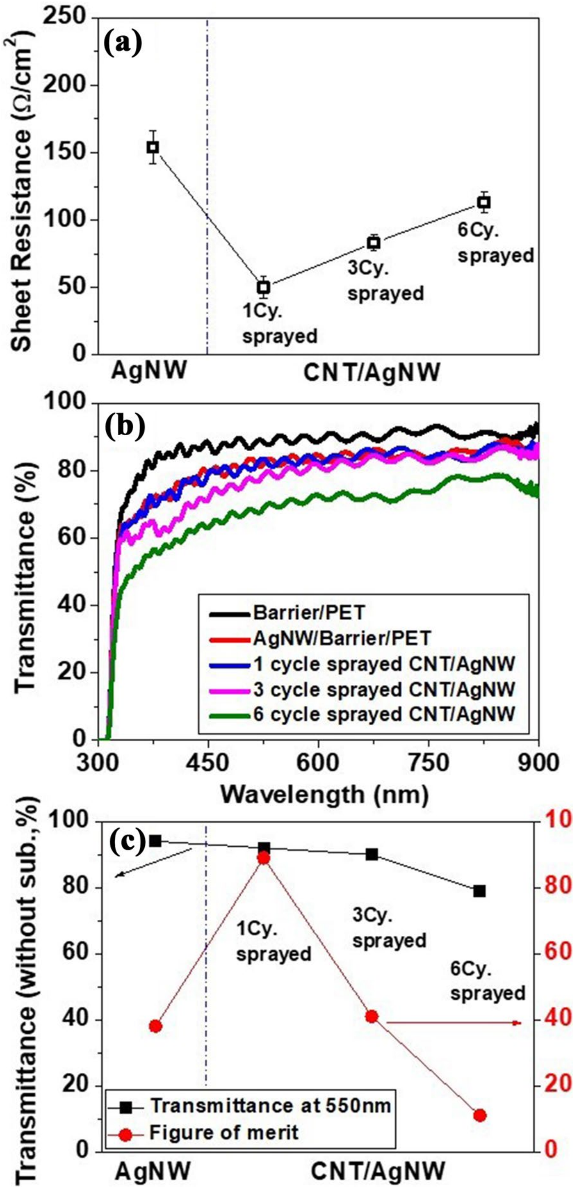

Fig. 1 **a** Sheet resistance of pristine spray-coated AgNW and CNT as a function of the number of spraying cycles on a AgNW film. **b** Optical transmittance of pristine AgNWs and CNTs as a function of the number of spraying cycles on AgNW film. **c** FoM of a AgNW and CNT as a function of the number of spraying cycles on a AgNW electrode calculated from the sheet resistance and optical transmittance

3 Results and Discussion

Figure 1a shows the sheet resistance (R_{sh}) of pristine spray-coated AgNWs, as well as CNTs sprayed onto the AgNW film in cycles. The R_{sh} of the AgNW film is 154 Ω/square. With one cycle of CNTs sprayed onto the AgNW film, the R_{sh} of a CNT/AgNW multilayer film is decreased significantly from 154 to 50 Ω/square. The increase in R_{sh} can be attributed to the improved contact resistance of the CNT–CNT junction with an increase in the number of cycles of CNT spraying onto the AgNW film. In addition, it is noteworthy that the error range also decreased with the CNT/AgNW multilayer films.

Figure 1b shows the optical transmittance of clean AgNW and CNT according to the number of spray cycles on the AgNW film. As the cycle of sprayed CNT/AgNW increases, the transmittance decreases.

For the AgNW film, the film transmittance is 94% at a 550 nm wavelength without a substrate, as shown in Fig. 1c. With one cycle of CNT spraying on an AgNW film, the film transparency is almost the same. Electrodes with an AgNW film undergoing one cycle of CNT spraying, and AgNW films on a barrier/PET substrate without such spraying, both showed good transparency within the visible wavelength. With an increase in the spraying cycle of CNTs, the CNT/AgNW multilayer electrode showed a decreased transmittance owing to the increased density of CNTs.

We calculated the figure of merit (FoM) using R_{sh} and the optical transmittance (T) of sprayed-AgNW and CNT/AgNW multilayer electrodes, as shown in Fig. 1c. We obtained the FoM by solving the following equation using the optical transmittance and R_{sh} from the literature:

$$T = \left(1 + \frac{188.5}{R_{sh}} \cdot \frac{\sigma_{OP}}{\sigma_{DC}}\right)^{-2} \text{ or FoM} = \frac{\sigma_{OP}}{\sigma_{DC}} = \frac{188.5}{R_{sh} \cdot \left(T^{-1/2} - 1\right)} \tag{1}$$

where σ_{OP} is the optical conductivity and σ_{DC} is the DC conductivity of the film. A higher FoM value indicates a better performance of the transparent electrodes. In this manner, it is easy to compare the quality factor of various transparent nanomaterial films. Owing to a lower sheet resistance and high transmittance of a single cycle of CNT spraying on an AgNW film at a 550-nm wavelength without a substrate, the CNT/AgNW multilayer electrodes demonstrated the highest FoM value of 89.

Figure 2 shows SEM images of AgNW and CNT/AgNW multilayer transparent conductive films under different spraying cycles. AgNW films are dispersed in isopropyl alcohol and then spray-coated onto barrier/PET substrates. In substrate, only PET can be peeled off for easy removal. By contrast, with a barrier on the PET, the majority of AgNWs are unable to be detached from the AgNW films. A barrier layer provides strong physical adhesion between the AgNWs. The barrier layer thickness is approximately 5 μm. Figure 2a shows an SEM image after six cycles of spraying of a AgNW film on the surface of a barrier/PET substrate. A randomly percolated network structure can be

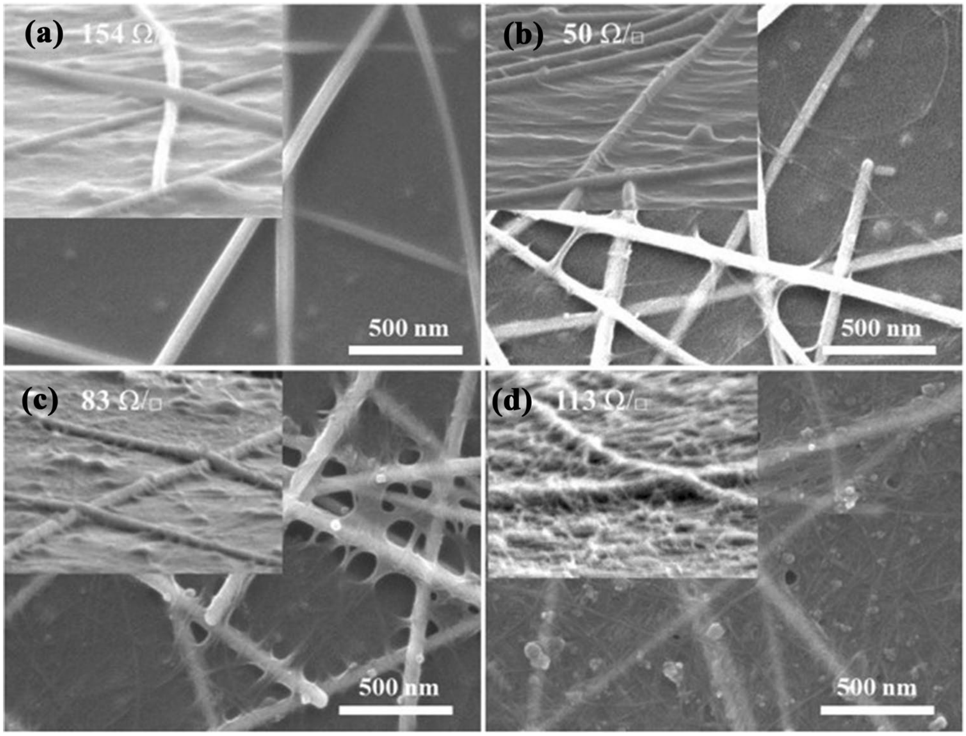

Fig. 2 Surface SEM images of pristine AgNW and CNT as a function of the number of spraying cycles on a AgNW film: **a** sprayed AgNW films, and **b** one **c** three, and **d** six cycles of CNT spraying on AgNW films. The insets show an off-angle view of each electrode

seen. The R_{sh} of the AgNW films is extremely large owing to the loose contact between the AgNWs.

With one cycle of CNT spraying on the AgNW films, after rinsing with deionized water for 1 minute, most of the SDS surfactant was removed, as shown in Fig. 2b. After one cycle of CNT spraying on the AgNW films, a CNT bundle formed around the AgNWs, binding the crossed AgNWs together. A CNT bundle can also be found between the AgNWs and barrier/PET substrate. CNT/AgNW multilayer films help significantly improve the film conductivity because CNT bundles bridge the AgNWs at their intersection and provide an improved conduction between the crossed AgNWs.

Three cycles of CNT spraying on AgNW films formed random networks and bundles of CNTs established between the AgNWs and filled in the intervening spaces, as shown in Fig. 2c. With six cycles of CNT spraying on the AgNW films, the films become fully covered with a CNT bundle, as shown in Fig. 2d.

Figure 3 shows the resulting AFM images of the surfaces of the AgNW and multilayer CNT/AgNW films after a spray coating cycle applied to the barrier/PET substrate. The root-mean-square (rms) roughness changes with an increase in the spray coating cycle. The rms roughness of the AgNW films with one, three, and six cycles of CNT spraying were 23.8, 21.4, 14.8, and 13.5 nm, respectively. The density of the CNTs increased with an increase in the number of spraying cycles. The CNT spraying resulted in a well-connected wire–wire junction and smooth surface. When OSCs are employed, the morphology of the film can increase the shunt resistance because the protruding CNTs can act as a leakage path. A low rms roughness and smooth morphology may decrease the shunt resistance of the OSCs.

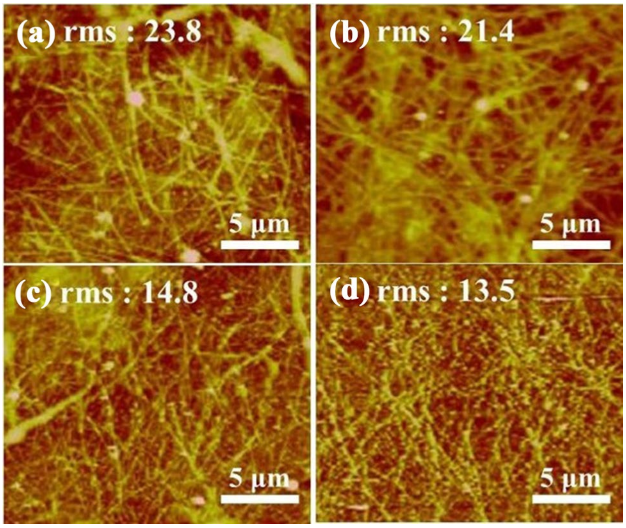

Fig. 3 AFM surface images of AgNW film and CNT as a function of the number of spraying cycles on AgNW film: **a** sprayed AgNW films, and **b** one, **c** three, and **d** six cycles of CNT spraying on AgNW films

To investigate how the R_{sh} of CNT/AgNW multilayer electrodes affects the performance of the OSCs, P3HT:PCBM/PEDOT:PSS-based devices were prepared

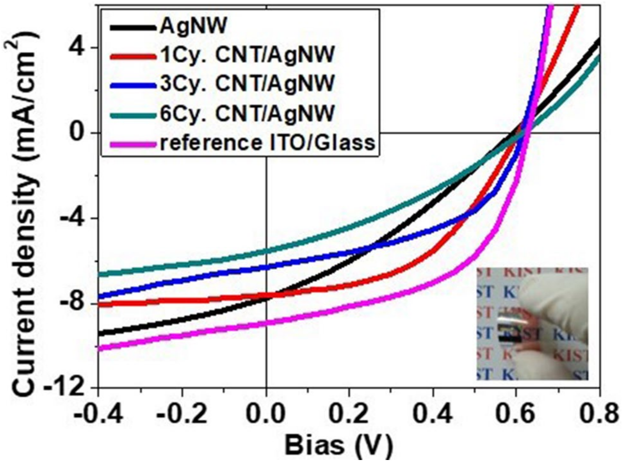

Fig. 4 J–V curves of OSCs fabricated on CNT/AgNW hybrid electrodes, where the insert shows the flexibility of the OSCs with different spray cycles of CNT/AgNW hybrid electrodes

and compared, as shown in Fig. 4. The inset in Fig. 4 shows the flexibility of the fabricated OSCs. A highly conductive PEDOT:PSS (Baytron PH1000) was recently used as a polymer anode to replace the ITO in OLEDs and OSCs. In some cases, highly conductive PEDOT:PSS showed a level of efficiency comparable to that of ITO-based devices. It is extremely important to increase the conductivity of the anode. A highly conductive PEDOT:PSS leads to an increase in the short-circuit current. The Efficiency of a solar cell is sometimes defined in terms of the fill factor (FF) which is defined as the ratio of area defined by (V_{max}, I_{max}) to the area defined by (V_{oc}, I_{sc}) on the I-V curve. As shown in Fig. 4, the current density–voltage (J–V) characteristics of a cell with a 154 Ω/square single AgNW electrode showed a FF of 31.11%, short-circuit current densities (J_{sc}) of 7.76 mA/cm^{-2}, an open-circuit voltage (V_{oc}) of 0.594 V, and a power conversion efficiency (PCE) of 1.43%. This somewhat low cell performance could be due to the low Rsh. By contrast, OSCs with 50 Ω/square CNT/AgNW multilayer electrodes showed an excellent OSC performance with an FF of 48.05%, a Jsc of 7.60 mA/cm^{-2}, a V_{oc} of 0.606 V, and a PCE of 2.21%. The PCE obtained is still low compared with the ITO on a glass cell showing a PCE of 2.95%, FF of 52.64%, J_{sc} of 8.94 mA/cm^{-2}, and V_{oc} of 0.627 V. The device with three and six cycles of CNTs sprayed onto AgNW electrodes exhibited cell performances with an FF of 48.13% and 32.88%, J_{sc} of 6.31 and 5.56 mA/cm^{-2}, V_{oc} of 0.614 and 0.615 V, and PCE of 1.86% and 1.12%.

Solar cells with AgNWs, CNT/AgNW multilayer anodes, and ITO devices show almost the same V_{oc}, although the fill factors are significantly different. The fill factor depends on the series resistance (R_s) of the solar cells. Here, the high R_{sh} of the electrode may reduce the fill factor. The low R_s (≈ 0) of the electrode in the photovoltaic devices substantially improves the fill factor. Normally, J_{sc} does not change significantly with an increase in the R_s, and only starts to change with an extremely large R_s, as in the present case. The decreased J_{sc} can be explained by the decreased optical transmittance of a CNT/AgNW multilayer electrode with an increase in the number of cycles of CNT spray coating.

4 Conclusion

CNT/AgNW multilayer electrodes fabricated using a simple spray deposition method were demonstrated. A CNT/AgNW multilayer electrode exhibited a R_{sh} of 50 Ω/square with a transparency of 94% at 500 ~ 550 nm wavelength without substrate. The CNT bundle formed bridges between the crossed AgNW contacts and filled in the intervening spaces, thus resulting in a high conductivity of the multilayer transparent electrodes. With the use of CNT/AgNW multilayer electrodes, the flexible polymer solar cell showed a high cell efficiency of 2.21%. Replacing the ITO, sprayed CNT/AgNW multilayer electrodes will advance the realization of inexpensive mass-produced and highly efficient flexible polymer organic solar-cell based films using a roll-to-roll based process.

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