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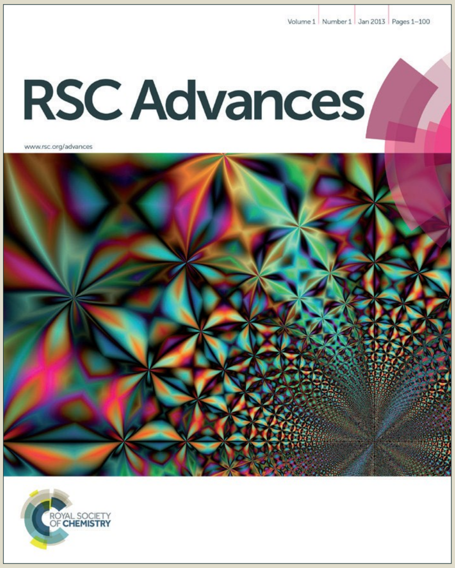

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High-performance flexible transparent electrode films based on silver nanowire-PEDOT:PSS hybrid-gels

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KEYWORDS

Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), 20-nm Silver nanowire, Hybrid gel, Transparent electrode, Solution-process, Organic photovoltaic cell

Abstract

We have developed highly transparent and electrically conductive hybrid-gel films based on poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and thin silver nanowires (Ag NWs) with diameters of 20 nm. Ionic gels based on PEDOT:PSS are a ionic conductors consisting of anionic PSS and cationic PEDOT. Ag NWs were combined with the conductive PEDOT:PSS chains, to assemble electrically conductive gels. The hybrid-gel films were created with a structure that incorporates Ag NWs into the conductive PEDOT chain matrix. We found that the conductivity significantly increased with Ag NW content. The optimized Ag NW-PEDOT:PSS hybrid-gel films exhibited excellent performance with a high transmittance of 92% and small haze of 1.1% at a low sheet resistance of 20 $\Omega\cdot sq^{-1}$, and good mechanical flexibility. Because of the high-performance, it is believed that the Ag NW-PEDOT:PSS hybrid-gel electrodes are highly suitable for practical use in flexible electronics.

INTRODUCTION

Flexible transparent electrode films (FTEFs) have recently attracted a great deal of attention for use in many optoelectronic devices such as large-area touch screens, thin-film solar cells, and organic light emitting diodes. Among these applications, the most commonly used materials is indium tin oxide (ITO), which has a high transparency and conductivity when used as the electrode layer for flexible display devices. At present, ITO-sputtered plastic films are generally used for practical applications[1] due to their low resistivity on the order of 10^{-4} Ω cm (sheet resistance as low as 50 $\Omega\cdot sq^{-1}$) and high optical properties up to 90% transmittance with ~1% haze. However, the high-conductivity ITO used in these FTEFs is particularly costly due to the slow coating rates and high temperature/vacuum processing conditions involved with sputtering. In addition, they also have brittle nature and are easily broken down by externally applied bending forces.[2] To further improve the flexibility of optoelectronic devices, flexible electrode materials of a different type are needed. Therefore, research into solution-coating alternatives to ITO that can be fabricated at high speeds, require low-cost processing conditions, and provide comparable performances is required. To find a substitute for ITO, great efforts have been made to develop new flexible transparent conductors such as poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS)[3-9], single-welled carbon nanotubes,[10-11] graphene,[12] and networks of silver nanowires (Ag NWs).[13-18] Only commercially available Ag NWs have demonstrated an optoelectronic performance that enemy that is comparable to that of ITO. Thus, Ag NW electrodes have been gaining interest as excellent candidates for transparent electrodes and promising alternatives to ITO due to their ease of manufacture, large-scale solution-coating, and high optical and electrical properties with mechanical ductility.[19-21] This good optoelectronic performance of Ag NW network films can be attributed that Ag NW network has high contact resistance by the wire-wire junctions. However, some properties of these Ag NW network films, such as the optical haze value, thermal stability, and plurality of film coating, are not desirable for flexible. Additionally, with respect to Ag NW network films, an optoelectronic performance that exceeds that of ITO has not been reported. Therefore, in order to improve the flexibility or bending for flexible optoelectronic devices further, different types of stretchable materials are needed. In particular, new electrode materials with conductivities and optical properties that are superior of those of ITO must be developed. As a method for solving these problems of Ag NW network film, the two-layered hybrid films have demonstrated that the hybrid conducting layer of Ag NWs with high surface uniformity and improved thermal stability can be obtained by embedding them into the PEDOT:PSS through the plurality coating technique.[22, 23] As a result, the two-layered hybrid films, which Ag NWs embedded into the PEDOT:PSS, were fabricated, and these optoelectronic performance were improved than Ag NW itself. Recently, Wang *et al*[24] have reported that the polysiloxane-PEDOT:PSS nanocomposite solution were fabricated by mixing a sol-gel modified polysiloxane with the aqueous PEDOT:PSS colloidal solution, and a polysiloxane-PEDOT:PSS-Ag

NWs hybrid solution was obtained by adding 90-nm-diameter Ag NWs to the nanocomposite solution, and after film casting, the optoelectronic property of these hybrid film was reached to 25 $\Omega\cdot sq^{-1}$ with ~80% transmittance. Kim *et al*[25] have also reported on the one-step coating technique of an Ag NW-PEDOT:PSS hybrid film by using neutralized PEDOT:PSS solution by adding imidazole as a mild base, and the resulting roll film showed the sheet resistance of ~75 $\Omega\cdot sq^{-1}$ with ~90% transmittance and 1.21% haze value. Anyway, the electrode materials having excellent conductivity and optical properties comparable to those of the ITO did not get.

In this report, we have developed highly conductive hybrid-gel films using PEDOT:PSS ionic gel and ultrathin Ag NWs with diameters of 20-nm. A hybrid-gel based on PEDOT:PSS is an ionic conductor consisting of anionic PSS and cationic PEDOT. Ag NWs are connected between the ionic conductive PEDOT chains, to assemble the electrical conducting gels. PEDOT itself is a well-known linear conducting polymer, which can be used to fabricate a conducting matrix, and it has been found that divalent cations efficiently promote the gelation with PSS due to the formation of secondary chemical bonds between the sulfonate group and sulfur atom on adjacent chains. PEDOT:PSS may be a good material for optoelectronic devices owing to its high intrinsic conductivity, up to 2000 $S\cdot cm^{-1}$,[3] although lower than that of the ITO or networks of Ag NWs, and electrochemical stability while maintaining moderate transparency and good film-forming properties. In this study, ultrathin Ag NWs with diameters of 20-nm are interconnected with the conducting PEDOT:PSS ionic gels, to assemble transparent and highly conductive materials. This hybrid-gel solution can be coated directly onto the polyethylene terephthalate (PET) substrate by a common solution-coating technique. The coated Ag NW-PEDOT:PSS hybrid-gel electrodes films exhibited extremely uniform surfaces with compact morphologies without any uneven or rugged surface. These properties are due to NWs that are embedded into the conducting PEDOT:PSS matrix, which have excellent flexibility. The chemical structure of the conductive Ag NW-PEDOT:PSS hybrid-gel electrodes is showed in Figure 1. An electron can be transferred from the charged Ag NWs to the cationic PEDOT chains and/or, subsequently, from the PEDOT chains to the Ag NWs. Overall, a metallic state can be achieved by the hybrid matrix. As a result, we obtained a hybrid-gel electrode layer that showed a high-performance with a high transmittance of 92% and small haze of 1.1% at a low sheet resistance of as little as 20 $\Omega \cdot sq^{-1}$. These properties are comparable to the optoelectronic performance of ITO.

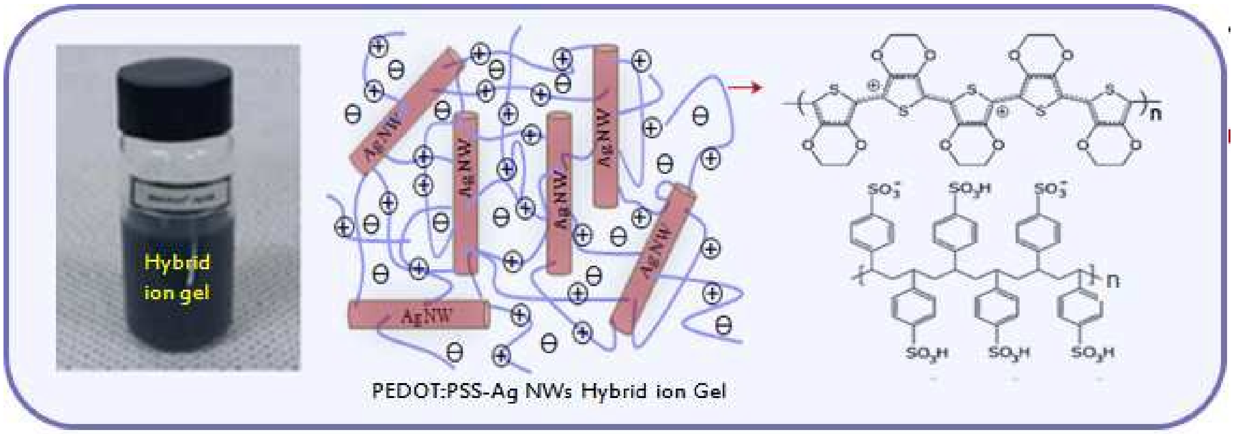

Figure 1. Chemical structure of conductive Ag NW-PEDOT:PSS hybrid-gel electrodes. The ionic gel based on PEDOT:PSS is an ionic conductor consisting of anionic PSS and cationic PEDOT. Thin Ag NWs with diameters of 20-nm connect the ionic conductive PEDOT and PSS chains.

EXPERIMENTAL SECTION

High-purity, ultrathin Ag NWs (average 20-nm in diameter, 22-μm in length) were directly synthesized through a high-pressure polyol method by chemical reduction of $AgNO_3$ (Aldrich) with polyvinylpyrrolidone (PVP) (average molecular weight, M_w=1,300,000, Aldrich) as a capping agent, and in the presence of a combined salt solution (NaCl and KBr) according to our previous paper.[26] The synthesized Ag-NWs were dispersed in the water solution (0.5wt% in H_2O) with a PVP (0.05wt% in H_2O, M_w=40,000, Aldrich) polymer surfactant.

To produce the ionic gels, 30 mL of the PEDOT:PSS (1.3% solution in water, Clevious PH 1000) was mixed with 80 mL of methanol, 5mL of dimethylsulfoxide (DMSO), 2.5 mL of ethylene glycol (EG), and silane series coupling agent as a first step. For the second step, PEDOT:PSS dispersion were heated to 85°C for 12 hr, and, ionic gels of PEDOT:PSS are formed and, cool to room temperature. Ag NW-PEDOT:PSS hybrid-gels were prepared as follows: PEDOT:PSS ionic gels were cooled to 5°C with vigorous stirring, and then the Ag NW solution was added so that the hybrid solution contained a 1:1 ratio of Ag NWs to PEDOT:PSS. These hybrid-gel ink solutions were coated directly onto the PET substrate in a one-step process using a Meyer bar. The highly conductive Ag NW electrode films were fabricated without any post-treatment. The morphology and molecular structures of the Ag NW-PEDOT:PSS hybrid-gel films were observed by field emission scanning electron microscopy (FE-SEM, JEOL-JSM5410) and transmission electron microscopy (TEM, JEOL-JEM2100F). The optical properties were measured by ultraviolet spectroscopy (UV/vis, SHIMAZU-UV3150) and using a Haze meter (NDH 7000). The electrical properties of the Ag NW-PEDOT:PSS hybrid gel films were measured using a standard four-point probe technique (Laresta GP, MCP-T60).

Flexible organic photovoltaics (OPVs) were fabricated onto hybrid electrode layer/PET substrates. For the conventional device are a architecture, 18 mg of poly(3-hexylthiophene) (P3HT) (Rieke metals, Inc.) and 10.8 mg of [6,6]-phenyl-C61-butyric acid methyl ester ($PC_{60}BM$) were dissolved in 1 mL of chlorobenzene; the solution was spin coated at 2500 rpm for 40 s and annealed at 150 °C for 13 min in a glove box. The thickness of the active layer was approximately 100 nm. For the reference devices, ITO electrodes on glass substrates (JMC Glass, 20 $\Omega\cdot sq^{-1}$ at 91% transparency) were used; all fabrication processes were identical. Solar cell properties were measured with a solar simulator (ORIEL) with a 450 W light source. The standard light source was calibrated by a standard Si photodiode to obtain the AM 1.5 condition and an intensity of 100 $mW\cdot cm^{-2}$.

RESULT AND DISCUSSION

The Ag NW-PEDOT:PSS hybrid-gel was composed of thin Ag NWs with diameters of 18-22 nm and PEDOT:PSS ionic conductors consisting of anionic PSS and cationic PEDOT. The Ag NWs were combined with the ionic conductive polymer PEDOT:PSS chains to assemble electrical conducting gels. Figure 2 shows representative SEM surface morphologies in the manufacturing stage of the Ag

NW-PEDOT:PSS hybrid-gel electrodes. As shown in Figure 2, PEDOT doped with PSS, which is commercially available in the form of an aqueous dispersion as colloidal gel particles, is one of the most successful conducting polymers. PEDOT and PSS form a poly-ion complex between PEDOT cations and PSS anions through electrostatic interactions. The poly-ion complex disperses in water as a colloidal gel particle with a diameter of 30-60 nm, where hydrophobic PEDOT molecules aggregate to form physical cross-links between the PSS chains. To produce the ionic gels, PEDOT:PSS dispersed with methanol, DMSO, EG, and silane series coupling agents were heated to 80 °C for 12 h, and then, ionic gels of PEDOT:PSS were formed. The pH value of the resulting PEDOT:PSS ionic gel solutions showed the almost neutral as 7 to 7.5, and these ionic gel solutions has also good miscibility with Ag NWs and can maintain stable hybrid gel condition until 2-3 weeks in the storage conditions of 5-10°C. In addition, when these neutral-pH PEDOT:PSS gel has been hybridized with Ag NWs, it can be act to an advantage that can be greatly improved the oxidation problem of the Ag NWs. On the other hand, the conductivity of conductive coated film obtained from PEDOT:PSS ionic gel solution alone can be obtained a sheet resistance of approximately 280-300 ohm/sq with 95% transmittance (PET film base). These conductivity value of PEDOT:PSS ionic gel film will be decreased by approximately two times compared to that from the pure conventional PEDOT:PSS dispersed solutions. However, ionic gels based on PEDOT:PSS were made from the PEDOT:PSS colloids, and Ag NWs were combined between the ionic conductive PEDOT and PSS chains through a hybridization process. As a result, Ag NWs were hybridized with the ionic PEDOT:PSS gels, which exhibited electrical conductivity, as shown in Figure 2. The 20-nm-diameter Ag NW-PEDOT:PSS hybrid-gel electrode layer was obtained, in which the NWs were embedded into the conducting PEDOT:PSS ion gel matrix, and these surfaces exhibited extreme uniformity with compact morphologies.

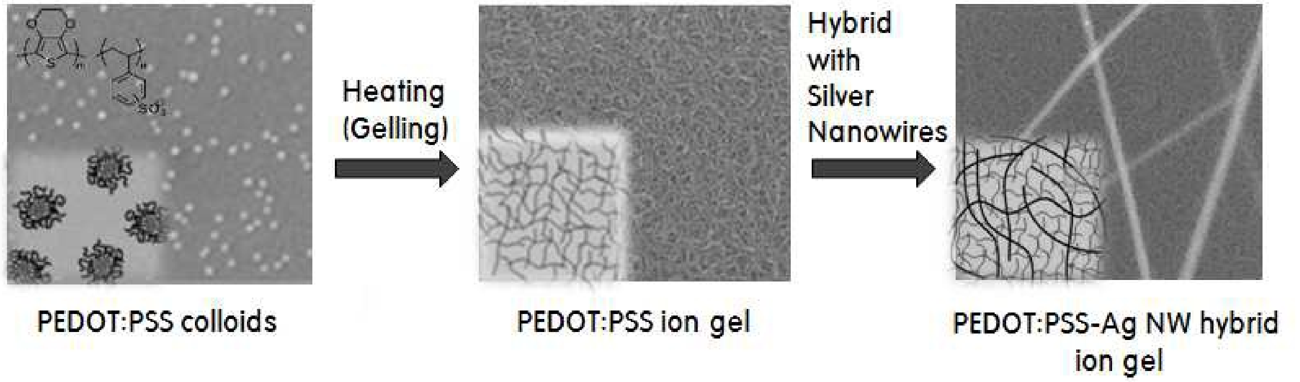

Figure 2. SEM surface morphologies in the manufacturing stage of 20-nm Ag NW-PEDOT:PSS hybrid-gel electrodes. Ionic gels based on PEDOT:PSS were made from the gelling of PEDOT:PSS colloids, and Ag NWs were combined between the ionic conductive PEDOT and PSS chains through a hybridization process.

The Ag NW-PEDOT:PSS hybrid-gel ink could be coated directly onto the plastic substrates using a Meyer bar or roll-to-roll slot die coater for film formation. The cross-sectional schematic and surface morphologies of the solution-coated Ag NW-PEDOT:PSS hybrid-gel electrodes films using the Meyer bar are shown in Figure 3. As shown in the SEM and AFM images in Figure 3, these hybrid conductive layers exhibited a compact, cross-linked morphology, and their roughness was less than 5 nm. Since this hybrid matrix layer consisted of the cationic PEDOT chains interconnected with charged Ag NWs, the size and density of the Ag NWs, in particular, seems to affect the electro-optical properties of the film significantly.

The effective conductivity, and sheet resistance ($\Omega\cdot sq^{-1}$), of the hybrid-gel layer, according to the wire contents, is shown in Figure 4. As shown in Figure 4-(1), the sheet resistance for the PEDOT:PSS gel matrix film alone was shown to be 270 $\Omega\cdot sq^{-1}$ at 94 % transmittance (PET film base). However, the hybridized PEDOT:PSS matrix films consisting of 1.5, 2.5, 3.5, 5, 10, 15, and 30 wt % Ag NWs resulted in improved conductivity with values of 192, 153, 120, 100, 55, 38, and 22 $\Omega\cdot sq^{-1}$, respectively, at 94 % transmittance. Thus, the sheet resistance of the hybrid-gel electrode film was greatly reduced when the wire content increased. In particular, the sheet resistance of the hybrid-gel films composed of 1.5wt% Ag NWs (Figure 4-(2)) was measured at 192 $\Omega \cdot sq^{-1}$ lower than that of the conductive PEDOT:PSS itself (270 $\Omega \cdot sq^{-1}$). This means that the charge transport or hopping occurred between the cationic polymer chains and the wires although there are no wire-wire junctions in the PEDOT:PSS gel matrix embedded with a small amount of Ag NWs. However, for the hybrid films consisting of more than 15wt% Ag NWs, all wires embedded into PEDOT:PSS matrix were connected to wire-wire junctions and interconnected with PEDOT chains, the conductivity, overall, was significantly improved. Finally, the hybrid films consisting to 30wt% Ag NWs exhibited good conductivity with a sheet resistance of 22 $\Omega \cdot sq^{-1}$ at 94 % transmittance (Figure 4-(8)).

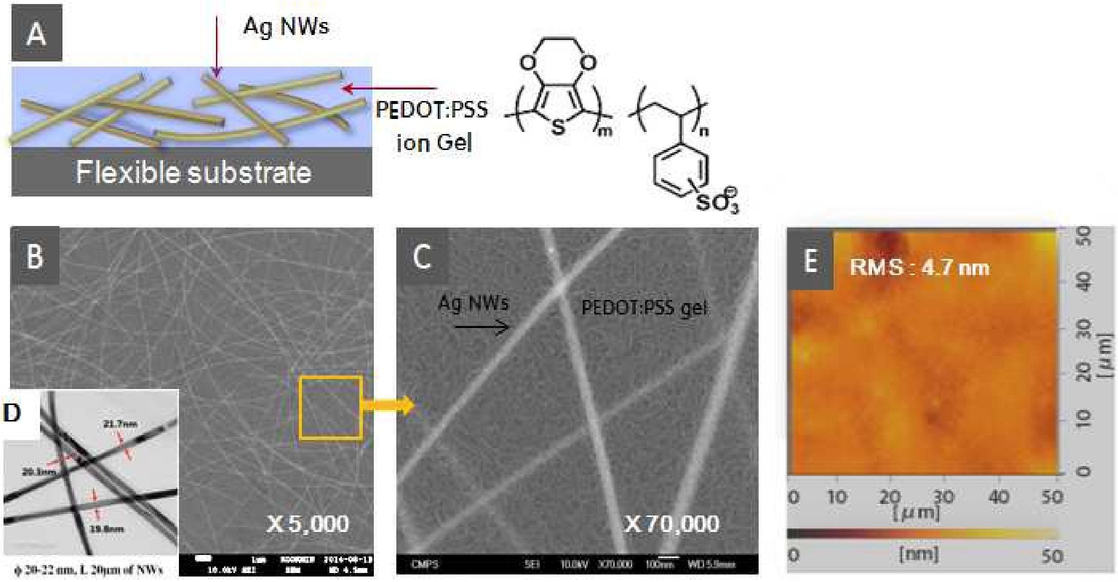

Figure 3. (A) Cross-sectional schematic of the Ag NW-PEDOT:PSS hybrid gel film, SEM morphologies at (B) low magnification (×5000) and (C) high magnification (×70 000), and (E) AFM image of hybrid-gel film directly coated on a PET substrate using Meyer bar, (D) TEM image of the 20-nm-diameter Ag NWs used in the hybridization with the PEDOT:PSS gel.

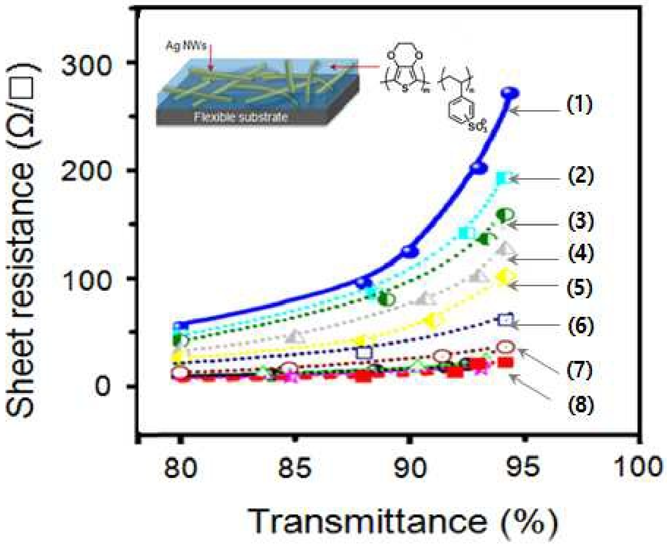

Figure 4. The sheet resistance-transmittance curves for the Ag NW-PEDOT:PSS hybrid gel layers: (1) PEDOT:PSS gel layer alone, and Ag NW-PEDOT:PSS hybrid-gel layers composed of (2) 1.5, (3) 2.5, (4) 3.5, (5) 5, (6) 10, (7) 15, and (8) 30 wt% Ag NWs. The inset is an embedded schematic of the Ag NW-PEDOT:PSS hybrid-gel layer.

Figure 5-(A) shows a plot of specular transmittance (%T, λ = 550 nm) versus sheet resistance ($\Omega \cdot sq^{-1}$) for films of Ag NW-PEDOT:PSS hybrid-gel electrodes composed of 30 wt % Ag NWs, along with data from previous literature results[1] for transparent conductors. As shown in Figure 5-(A), the transmittance of the hybrid-gel films made in this work was up to 5-10% greater than films made from the network structure of NWs only, and showed at least equal performance to the sputtered crystalline ITO on glass. However, the hybrid-gel electrodes in this work could achieve a low sheet resistance of 20 $\Omega \cdot sq^{-1}$ at a transmittance of 92 %, their haze value was also controlled to the 1.1% level (PET film base) at a low sheet resistance of 20 $\Omega \cdot sq^{-1}$ suitable for electronic display applications. This electrical performance matches the properties of crystallized-ITO films, and in optical performance, their transmittance and haze values are almost the same as that of ITO films. Here, the thin Ag NWs with a mean diameter of 20-nm and lengths of 22-μm were prepared by a high-pressure polyol process.[26] Purified Ag NWs were transferred into H_2O based-ink solution containing 0.1% ethyl cellulose for coating with a Meyer bar. The performance of the Ag NW films

was considered to be good with a transmittance of 88-89 % at a low sheet resistance of 20 $\Omega\cdot\text{sq}^{-1}$, as it is indicated in Figure 5 (A); however, their performance was not as good as that of the hybrid films. In addition to the excellent transparency and electrical conductivity, the hybrid-gel electrode films possessed good flexibility, which is essential for emerging optoelectronic flexible devices. To improve the mechanical flexible stability of the hybrid-gel electrode films, the resistance of the electrode film was changed according to the bending cycle number showed in Figure 5-(B). The test system consisted of two contact lines: one of the lines was fixed and the other could be moved laterally. In this test, the bending was rolled at a distance with diameter of 10 mm, subsequently unrolled at speed of 20 mm s^{-1}, and the sheet resistance of the electrode film (R) was compared to its initial value (R_0). In the case of the hybrid electrode film used in this work, the change of sheet resistance (R/R_0) could be expressed as 1% or less after being unrolled 2000 times. On the other hand, the ITO electrode film used as a reference showed significant changes after less than 20 repetitions and severe cracks formed on the film surface, as shown in Figure 5 (B).

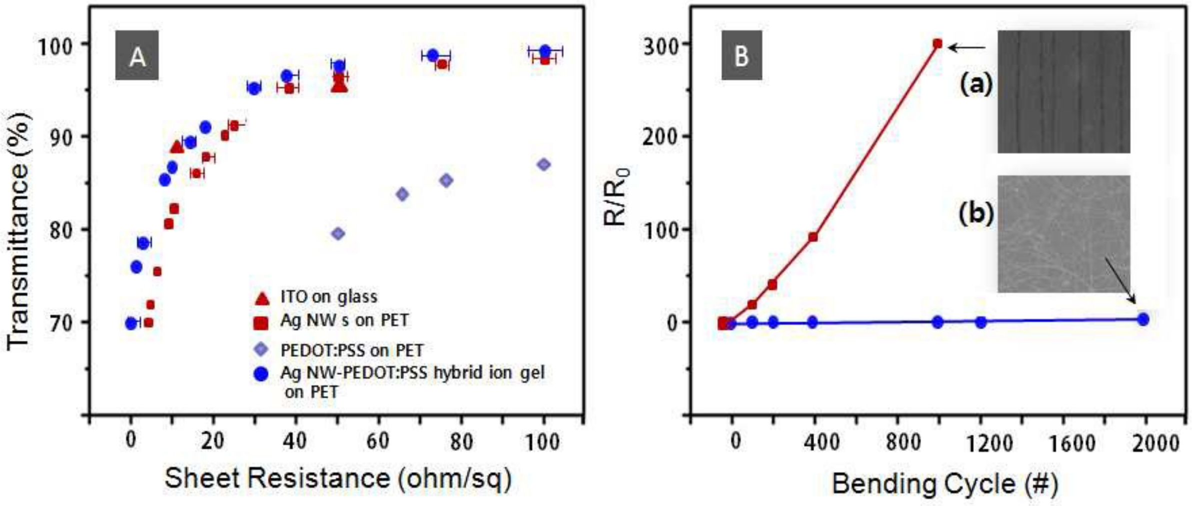

Figure 5 (A) Plot of transmittance (λ = 550nm) versus sheet resistance for a 20-nm-diameter Ag NW-PEDOT:PSS hybrid-gel film. Error bars show one standard deviation for five measurements. The performances of ITO,[1] 20-nm-diameter Ag NWs only, and PEDOT:PSS gel are shown for comparison. (B) Change of sheet resistance after a bending test of 2000 cycles: (a) ITO electrode on PET film for comparison and (b) 20-nm-diameter Ag NW-PEDOT:PSS hybrid-gel electrode film.

There are necessary criteria for transparent electrodes with a flexible substrate, to be used in OPV devices or organic light-emitting diodes (OLED). In particular, to achieve sufficiently transparent electrodes, films must have a high transparency of more than 90 % (level of ITO) with 30 $\Omega\cdot sq^{-1}$ sheet resistance for device applications, and a low haze value. If transmittance and haze value can be achieved at the same conductive range as for ITO, hybrid-gel electrodes will offer new capabilities for OPV or OLED applications. In order to investigate the performance for practical application of the electrode films made by 20-nm-diameter Ag NW-PEDOT:PSS hybrid-gel electrodes in flexible OPVs, cells were fabricated based upon the following architecture: 125 μm PET film/hybrid-gel layer/ZnO/PEIE/P3HT-PCBM/MoO_3-Ag (PEIE = polyethyleneimine, PCBM = [6,6]-phenyl C_{60} butyric acid methyl ester). Figure 6 shows the current density-voltage (*J-V*) characteristics of flexible OPVs with Ag NW-PEDOT:PSS hybrid-gel electrodes, as well as a rigid ITO electrode device for reference, measured under AM 1.5 G illumination and in the dark. Ag NW-PEDOT:PSS hybrid-gel films with a sheet resistance of 20 Ω sq^{-1} were used as the electrodes for the fabrication of experimental flexible OPVs, and the resulting efficiencies were comparable to those of the conventional ITO electrodes on glass. Having investigated the Ag NW-PEDOT:PSS hybrid-gel film obtained by a solution-coating technique using a Meyer bar, small-molecule OPV cells were built using these electrode films. The 100-nm-thick ZnO, 15-nm-thick PEIE, and a 200-nm-thick bulk hetero-junction layer composed of P3HT and PCBM was then spin coated in a glove box. The cell used the fundamental structure of the OPV device (as shown in Figure 6) with a bulk hetero-junction absorber layer composed of P3HT:PCBM, commonly used in organic solar cells.

The photo-current density (J_{sc}) versus applied voltage (V_{oc}) characteristic under illumination and the solar cell performance are summarized in the *J-V* curve and in the table in Figure 6, respectively. The reference device with an ITO electrode on glass (with a sheet resistance of 20 $\Omega\cdot sq^{-1}$) exhibited a power conversion efficiency (PCE) of 2.76 % and a fill factor (FF) of 0.57. On the other hand, the cell using the Ag NW-PEDOT:PSS hybrid-gel film on PET fabricated in this work exhibited a PCE of 2.62% and a FF of 0.47, comparable to the reference ITO on glass. However, the OPV cell using the Ag NW-PEDOT:PSS hybrid-gel electrode exhibited a PCE of 2.62%, slightly lower than that of the ITO-electrode on glass because the fill factor on the Ag NW-PEDOT:PSS hybrid-gel electrode is smaller than that on ITO. These results can be attributed to the fact that devices using a Ag NW-PEDOT:PSS hybrid-gel electrode layer should be formed by a wet-coating technique to realize a higher uniformity or surface roughness and a more compact organic layer in order to maintain the efficiency at a level comparable to the sputtered-ITO device.

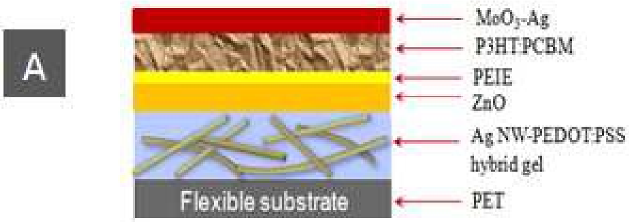

Table 1

	V_{oc} (V)	J_{sc} (mA/cm²)	FF	PCE (%)
ITO (Ref.)	0.58	8.23	0.57	2.76
Ag NW-PEDOT Hybrid	0.57	9.79	0.47	2.62

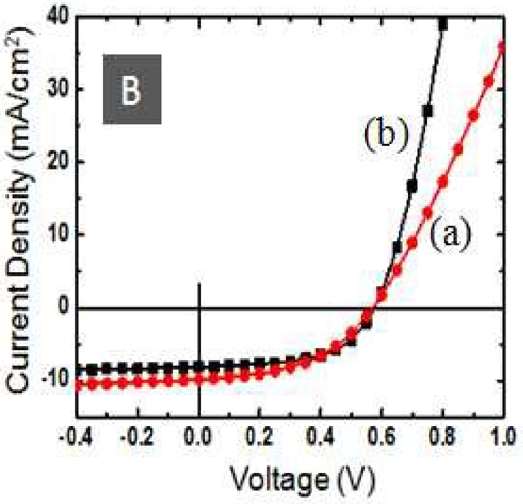

Figure 6 (A) Device structure of the flexible OPV using a Ag NW-PEDOT:PSS hybrid gel electrode, (B) the current density-voltage characteristics of the OPV: (a) Ag NW-PEDOT:PSS hybrid gel electrode on PET film in this work and (b) ITO-electrode on glass. The table is a summary of the performance of the Ag NW-PEDOT:PSS hybrid-gel electrode and ITO-electrode solar cells.

CONCLUSION

We have investigated highly transparent and electrically conductive hybrid-gel films based on PEDOT:PSS and Ag NWs with diameters of 18-22 nm, that were fabricated by a one-step wet-coating technique. Improved conductive PEDOT-based electrode films were assembled by hybridization with charged Ag-NWs. The hybrid layers consisting of PEDOT chains interconnected between random Ag-NW networks were found to have better conductivity and transmittance than PEDOT alone or pure Ag NW networks. The optimized Ag NW-PEDOT:PSS hybrid gel films, consisting of 30wt % Ag NWs, exhibited excellent performance with a low sheet resistance of 20 $\Omega \cdot sq^{-1}$ at 92% transparency, which is comparable to the properties of ITO-electrodes. Furthermore, the highly flexible Ag NW-PEDOT:PSS hybrid-gel transparent electrodes were also supported on a PET film using a conventional wet coating technique. As a result, a flexible photoelectric conversion was observed when the electrodes were incorporated into OPV cells. The OPV cell devices deposited onto these hybrid electrodes performed equivalently to devices based on a conventional ITO electrode. By virtue of the high-performance, it is believed that the Ag NW-PEDOT:PSS hybrid ion gel electrodes are highly suitable for practical use in flexible electronics.

ACKNOWLEDGMENT

This work was financially supported in part by the Industrial Core Technology Development Project through the Ministry of Knowledge and Commerce (10035644).

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