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ARTICLE

Highly Reliable AgNW/PEDOT:PSS Hybrid Films: Efficient Methods for Enhancing Transparency and Lowering Resistance and Haziness

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Silver nanowire (AgNW) is a remarkable component that may be able to replace indium tin oxide (ITO) as a transparent electrode due to its high DC conductivity and excellent optical transmittance. However, a common coating method can cause detrimental electrical deviation and poor optical properties due to the creation of randomly organized connections of AgNW. These problems should be overcome in AgNW-based films for transparent and reliable conductive electrodes through material and engineering approaches. In this work, we demonstrated highly conductive films of an AgNW/PEDOT:PSS composite with an excellent optical transparency and good electrical deviation through a multi-layer coating process with a controlled AgNW solution. We studied the effect of the number of coatings and optimized the process for high-performance AgNW/PEDOT:PSS composite films. The resulting film showed 2.3 % enhancement at 550 nm in terms of the transmittance and reduction of haziness from approximately two to four percent according to the number of coatings. In addition, the film exhibited an excellent electrical standard deviation of 1.7 Ω sq⁻¹ at all areas of the substrate in a reliability test. The optimized AgNW/PEDOT:PSS film was patterned by photolithography and etching processes to confirm the possibility for electrode applications and patterned film showed clear 30 µm width line patterns maintaining resistance. These improvements by our method can support new approach for transparent electrodes with excellent optical and electrical properties using metal-based nanomaterials.

1. INTRODUCTION

Recently, highly transparent conducting film has become a critical component for optoelectronic devices such as organic light-emitting diodes (OLEDs),¹⁻⁴ touch panels,^{5, 6} and solar cells⁷⁻¹² because future display technology requires not only conductivity but also transparency. Indium tin oxide (ITO) is the most commonly used common transparent electrode due to its high optoelectronic performance.13 However, ITO has a number of drawbacks related to its ceramic nature. When deposited onto a flexible substrate, the brittleness of metal oxides leads to film cracking when the substrate is bent. These cracks can propagate, eventually leading to sharp decreases in the film's electrical conductivity.¹⁴ Furthermore, in cases where a transparent electrode is required on top of an organic active layer, the sputter deposition of ITO into an organic material is known to cause damage to the underlying organic layers, leading to a decrease in the performance of the device. Thus, in recent years, various attempts have been made to replace ITO. Several feasible alternatives have been studied, including highly conductive carbon nanotubes,^{15, 16} grapheme,^{17, 18} metal nanofibers,^{4, 19, 20} metal grids,^{21, 22} solution-based PEDOT:PSS

(poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)),^{3, 23,} and silver nanowire (AgNW).²⁵⁻²⁷ Carbon-based nanostructures are limited due to their low conductivity. In addition, it is especially difficult to form a film with large-area uniformity using currently available solution processes. However, metal-based nanomaterials can support excellent electrical conductivity, large-scale synthesis, and easy control of the shape. Among these materials, AgNWs have been shown to form high-quality electrode coatings from solution processes.^{28, 29} The AgNW film electrode has high transmittance in the visible wavelength region that is comparable to that of ITO, with similar sheet resistance characteristics. Furthermore, the broad range of high transmittance in the near-infrared range allows the AgNW electrode to be used in infrared solar cells. However, common AgNW electrodes are unsuitable for use in many device applications because their non-uniform random network structures lead to poor reliability, reflection, and haziness problems. Therefore, AgNW films should have not only low resistance but also good reliability and optical properties for optoelectronic applications. In fact, the AgNW conductive film

with intrinsically poor uniformity from an inhomogeneous AgNW solution is associated with a high degree of electrical deviation which can have serious drawbacks when used in the fabrication of highly efficient optoelectronic devices. Therefore, much effort has been devoted to achieving good uniformity of AgNW films by mechanical pressing,²⁷ polymer composition,^{12, 30} and by over-coating with PEDOT:PSS.^{5, 7, 31} In spite of these efforts, a fundamental and effective method for the fabrication of high-performance AgNW films has yet to be realized. To the best of our knowledge, studies focusing on AgNW film fabrication with excellent reliability at large scales, enhanced transparency, and very low haziness have not been reported. In this work, we introduce a multi-layer coating method for the fabrication of AgNW/PEDOT:PSS thin films. Our method offers an effective process for low electrical deviation, low haziness, and high transmittance. We expect that this method can be applied to spray coating, roll-to-roll coating, slot die coating and other coating processes for highperformance films.

2. EXPERIMENTAL

The AgNW solution used in this study was purchased from Nanopyxis (Korea) as a dispersion solution in isopropyl alcohol (concentration = 11.8 mg mL⁻¹). The average length and diameter of the AgNWs were 25 μ m and 45 nm, respectively. Poly(3,4-ethylenedioxythiophene)/ poly(styrenesulfonate) (PEDOT:PSS) PH1000 was purchased from Clevios. Dimethylsulfoxide (DMSO) and isopropyl alcohol were purchased from Aldrich and used without further purification. The PEDOT:PSS solution was mixed with 5 wt% DMSO, stirred at room temperature for 24 h, and used for the manufacturing of the hybrid films.

The AgNW solution was used without sonication because its aspect ratio changes during sonication. To create AgNW solutions with different concentrations, AgNW solutions were diluted at 1.4 wt% with isopropyl alcohol. The diluted AgNW solution was spin-coated onto O2-plasma-treated glass and PET substrates. The total quantity of AgNWs coated onto the substrates was fixed at both single- and multi-layer coatings. For the single-layered AgNW film, 1.4 wt% of AgNW solution was coated one time on the substrate by spin-coating at 5000 rpm for 40 sec and annealing at 150 °C for 5 min, while the multi-layered AgNW films were fabricated by means of two, three, four, and five instances of spin-coating using AgNW solutions with 0.7, 0.47, 0.35 and 0.28 wt% of AgNW, respectively. The PEDOT:PSS solution was sonicated for 2 min and filtered with 5 µm syringe filters before the spin-coating process. The resulting solution was spin-coated onto AgNW films at 5000 rpm for 40 sec. The film was then dried at 150 °C for 2 min under ambient conditions.

The transmittance spectra was obtained using a UV/Vis/NIR spectrophotometer (PerkinElmer, Lambda 750) and measured using bare glass and PET as the references. The haziness value was measured using a haze meter (Nippon Denshoku, COH-

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400, Japan). The sheet resistances were measured by the fourpoint probe method (Napson, RT-70V/RG-5) and were Fig. 1 (a-b) SEM images of the AgNWs used in the preparation of the conductive films

obtained as averaged values from 100 areas (glass substrate: 7.5 x 7.5 cm^2). The standard deviation values were obtained from 100 instances of data of different areas on the sample for the reliability evaluation (Fig. S1-S4). The thickness of the films was obtained by a surface profiler (Alpha step, Tencor Instruments, AS500). The density of the AgNW films was calculated using a microbalance (Shimadzu, AEG-45SM, resolution of 0.01 mg). Surface morphology images of the electrodes were analyzed by means of the FE-SEM (Jeol, JSM-6700F) and optical microscope (Leica, Polycon). AFM (Park System, XE-Bio) was used in non-contact mode for the topography characterization. The patterning of AgNW/ PEDOT:PSS thin film was carried out by photolithography process. The materials for photolithography process were supported by Dongjin Semichem Co., LTD. The photoresist (DayCon-PR) was spin-coated on AgNW/PEDOT:PSS thin film substrate at 2000 rpm for 30 sec. After coating process, the substrate was annealed at 110 °C for 90 sec. Then, the substrate was irradiated by UV source for 6 sec and developed by developer (MF310). After immersing for 8 sec, the substrate was washed with distilled water. The developed substrate was etched for 10 sec by using etchant (DayCon-AM) containing HNO3 and NaOCl. After that the remaining photoresist was stripped for 15 sec by stripper (DayCon-ST). Finally, patterned AgNW/PEDOT:PSS substrate was obtained after washing with distilled water.

3. RESULTS AND DISCUSSION

A pristine AgNW solution was spin-coated onto glass and dried

to confirm the diameter, length, and purity of the AgNWs. As shown in Fig. 1, the AgNW film showed a high degree of purity



Fig. 2 Electrical properties of the materials: (a) The sheet resistance of AgNW films according to the concentration of the AgNW-dispersed solution. (b) The conductivity of PEDOT:PSS films coated onto glass substrates according to the amount of DMSO. (c) The sheet resistance of AgNW/PEDOT:PSS hybrid films according to the concentration of the AgNW-dispersed solution. (e) Comparison of the electrical percolation behavior of AgNW and AgNW/PEDOT:PSS hybrid films according to the concentration of the AgNW-dispersed solution.

without particles, and the length and diameter were found to be $\sim 25 \ \mu m$ and $\sim 45 \ nm$, respectively, on average. The electrical properties of the AgNWs and PEDOT:PSS were characterized for optimization before the preparation of the multi-layered AgNW film (Fig. 2). The AgNW films were prepared as singlelayer films using AgNW solutions with different concentrations. The percolation threshold for single-layer AgNW is between 0.3 and 0.5 wt%, (Fig. 2b,c). In addition, the minimum sheet resistance was obtained in a saturated concentration of 1.4 wt% (Fig. 2a), therefore, the concentration of AgNW solution was fixed as 1.4 wt%. The sheet resistance and conductivity of the PEDOT:PSS were measured by varying the DMSO content from 1 to 10 wt%; as a known the value was saturated at 5 wt%. Therefore, PEDOT:PSS was mixed with 5 wt% DMSO for the coating process in this study. To confirm the effect of the PEDOT:PSS, it was coated onto AgNW film. The film showed a dramatically reduced percolation threshold from 0.3 to 0.05 wt% compared to that of single-layer AgNW (Fig. 2d,e). In this case, the incorporation of PEDOT:PSS on AgNW helped to reduce the remaining holes in the AgNW network and improve the film conductivity. Moreover, PEDOT:PSS, consisting of highly conductive nanoparticles, can provide an electron pathway between non-crossed AgNWs and improve the electrical field distribution,²⁷ as PEDOT:PSS serves as a conducting connector between the AgNWs.

Fig. 3a shows the sheet resistance difference between the AgNW film and the AgNW/PEDOT:PSS film at the same concentration of AgNW solution, exhibiting a large value at a low concentration of AgNW solution and saturation above 1.0 wt% because the AgNW is the main conductive channel, with



low resistance compared to PEDOT:PSS. The transmittance of the AgNW/ PEDOT:PSS film decreased linearly as the Fig. 3 (a) The sheet resistance differences (- \bullet -) between single-layer AgNW films and AgNW/PEDOT:PSS films and the transmittance at 550 nm (- Ψ -) according to the concentration of AgNW. (b) The standard deviation values of single-layer AgNW films and AgNW/PEDOT:PSS films according to the concentration of AgNW (Fig. S1 and S2).

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concentration of the AgNW solution increased. To create a reliable film with uniform resistance throughout the film area is very important for conductive films because a defect or nonuniform resistance of the films induces poor performance in



Scheme 1 Schematic illustration of the preparation process of the AgNW electrode and AgNW/PEDOT:PSS hybrid structure films by the single-coating and multi-coating methods. (i) One-step coating using AgNW-dispersed solution with a high concentration (1.4 wt%). (ii) Coating of PEDOT:PSS on AgNW-coated substrates at 5000 rpm. (iii) Coating process of AgNW-dispersed solution with a low concentration (0.28 - 0.7 wt%). (iv) Multi-step coating of AgNW-dispersed solution using the same concentration of AgNW solution used in (iii).

applications as an electrode. Therefore, the standard deviation values of AgNW and AgNW/PEDOT:PSS films created with a single coating were calculated and compared, as shown in Fig. 3b. To obtain a reliable standard deviation, the resistance values were taken and calculated from 100 different areas of the film (see the Supplementary Information). The AgNW film showed a nonuniform sheet resistance with a large standard deviation at low concentration of AgNW solution, but the value was reduced to 3.17 Ω sq⁻¹ at a high concentration. Interestingly, the PEDOT:PSS-coated hybrid composite films showed better uniformity with a lower standard deviation than only the AgNW films throughout the entire range, which indicates that the PEDOT:PSS connects the empty spaces of randomly coated AgNWs and enhances the degree of resistance uniformity. In addition, the AgNW/PEDOT:PSS composite film exhibited a lower standard deviation of 2.74 Ω sq⁻¹ compared to that of the AgNW film at a high concentration, showing that the PEDOT:PSS plays an important role in the reliability of conductive films.

Silver is an intrinsically reflective material, and AgNW is a light-scattering material.³² In addition, AgNW becomes randomly dispersed in a solvent; therefore, an inhomogeneous coating can cause problems such as haziness, transmittance, and electrical resistance during the fabrication of conductive film as an electrode. Furthermore, control of the concentration of AgNW is important when tuning the solution viscosity for a uniform coating because the mechanical disturbance and aggregation of AgNW during a wet coating process can stem from capillary forces during the solvent evaporation step.²⁷

To solve these problems, optimization of the coating process was carefully carried out. In fact, the AgNW solution with 1.4 wt% of AgNW is a very high concentration that can cause the



bulk silver zone to show relatively poor optical and electrical

properties. Thus, a multi-coating process with a diluted AgNW

solution was considered and compared to a single-coating

Fig. 4. (a) The sheet resistance and (b) the standard deviation values of AgNW and AgNW/PEDOT:PSS hybrid films according to the number of coatings of AgNW using AgNW solutions with different concentrations (Fig. S3 and S4). (c) The transmittance and haziness of AgNW/PEDOT:PSS hybrid films according to the number of coatings of AgNW using AgNW solutions with different concentrations.

AgNW coated onto the substrate was fixed by varying the coating number when AgNW solutions with different concentrations were used. First, the AgNW solutions were diluted with isopropyl alcohol to prepare the desired solutions with different concentrations. Then, the prepared solutions were spin-coated onto the substrate and dried at 150 °C. This process was repeated five times for the AgNW solution with a low concentration (0.28 wt%). Finally, PEDOT:PSS was coated onto the AgNW film and annealed to create a hybrid film. The performances of the AgNW and AgNW/PEDOT:PSS

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composite films as a function of the number of coatings are shown in Fig. 4. Fig. 4a shows that the single-coated AgNW film had the lowest resistance of $\sim 18 \Omega \text{ sq}^{-1}$ due to the large amount of AgNW (Fig. 5a). This value became saturated at ~ 21



Fig. 5. SEM images (a,d) of single-layer coated AgNW film using 1.4 wt%, (b,e) a film sample coated three times with AgNW with 0.47 wt% of AgNW-dispersed solution, and (c,f) a film sample coated five times with AgNW with 0.28 wt% of AgNW-dispersed solution. (g-i) Photographic images of AgNW/PEDOT:PSS hybrid films that PEDOT:PSS coated onto (a-c) AgNW films (glass substrate: 7.5 x 7.5 cm).

 Ω sq⁻¹ in the case of the multi-layered films. Furthermore, the PEDOT:PSS decreased the sheet resistance to about 4 Ω sq⁻¹ in all films. This was also noted at different AgNW concentrations. The reliability of the films was characterized using the standard deviation, as shown in Fig. 4b. The number of coatings decreased the standard deviation of the AgNW film decreased from ~ 4.2 to ~ 2.5 Ω sq⁻¹. In addition, the PEDOT:PSS reduced this value to less than 2 Ω sq⁻¹ in the multi-layered films, which is interesting as it showed that a multi-coating process and the introduction of PEDOT:PSS could decrease the standard deviation below 2 in all areas of films and thus lead to the creation of a highly reliable film sample. More interestingly, the transmittance was enhanced by 2.3 % at 550 nm and the haziness was reduced from \sim 4 to \sim 2 % according to the number of coatings. These are noteworthy improvements because the optical property is one of the key factors in the development of transparent electrodes (Fig. 4c). This indicates that the multi-layer coating enhances the optical properties of film due to the enhanced coating uniformity. As is well known, internal haziness is related to the diameter of AgNW and external haziness is related to the coating uniformity and gaps between the AgNWs.33 Therefore, good uniformity and organization between AgNWs can reduce the light scattering and total haze.³⁴ From these results, we can conclude that additional coatings will saturate the sheet

resistant at some point, but this process can strongly affect the reliability, transparency, and haziness. Therefore, the optimization of the coating process is very important. Moreover, a further increase in the conductivity can also be achieved by the incorporation of an organic conductive polymer, PEDOT: PSS in this case. A scanning electron microscopic (SEM) study can prove a performance enhancement by offering a morphological analysis of the AgNW density, connections, degree of dispersion, and degree of aggregation. The SEM images shown in Fig. 5a,d indicate that the single-layer film coated with the AgNW solution with a high concentration has aggregated and greatly overlapped networks between the AgNWs and a high quantitative density of 0.38 g m⁻², leading to low transparency and haziness (Fig. 5g). Fig. 5 b,c,e,f show that as the number of coatings increases, the network of AgNWs becomes well organized and the overlapped structure becomes significantly loose compared to the film created from a highly concentrated AgNW solution. In addition, the quantitative density of the AgNWs decreased from 0.38 to 0.34 g m⁻² as the number of coatings increased. Thus, these results clearly verify the improvement of the transparency and haziness of the films when the sheet resistance is not greatly different and when relatively long nanowires are ideally arranged and controlled, as shown in Fig. 4 and 5g-i. Also, we can conclude that the

proper quantity of AgNW is required for high-performance optical properties.

The surface topography and roughness of the hybrid composite films fabricated with different numbers of coating were characterized and compared using atomic force microscopy



Fig. 6 AFM topological images of (a) single-layer coated (1.4 wt% AgNW solution) and (c) hybrid films coated five times (0.28 wt% AgNW solution) with AgNW/PEDOT:PSS. AFM phase images of (b) films with a single-layer coating and (d) with five coatings.

(AFM). Fig. 6a,c show AFM topographical images of the AgNW/PEDOT:PSS composite films prepared with a singlelayer coating and with five coatings, respectively. Fig. 6a reveals many aggregated sites of AgNWs compared to the film created via the multi-coating process. Well-organized and welldistributed AgNWs are shown in the film fabricated with five coatings, and the AgNWs are excellently connected without serious aggregation compared to the single-layer coated film (Fig. 6b,d). These facts could be confirmed by the root mean square (RMS) roughness. The roughness was significantly decreased from 31.3 to 19.6 nm as the number of coatings increased. The surface roughness is very important when creating transparent electrodes because electrical shorts can be caused by protruding AgNWs.35, 36 Therefore, the low roughness value associated with the multi-layer coating can be critical when attempting to fabricate high-quality devices. Furthermore, our method offers better convenience of the fabrication process compared to the process used to create AgNW films with a high roughness value, as these films must undergo a mechanical pressing technique.²⁷

To confirm the effect of the multi-coating process of the hybrid film on the transmittance, films with different sheet resistance levels were fabricated by varying the total amount of AgNWs, as shown in Fig. 7a. The transmittance data was obtained at a wavelength of 550 nm, the transmittance was measured with a UV/Vis/NIR spectrometer with a bare glass as the reference. The multi-layer coated (five times) AgNW/PEDOT:PSS composite films showed higher transmittance values than the single-layer coated AgNW/PEDOT:PSS composites. The multilayered AgNW/PEDOT:PSS composite film exhibited transmittance of 90.8% and sheet resistance of 22 Ω sq⁻¹. The corresponding values for the single-layer coated AgNW/PEDOT:PSS films were respectively 88.6% and 23 Ω sq⁻¹. In addition, the sheet resistance of the single- and multi-layered AgNW/PEDOT:PSS films showed sheet resistance values of 88.3 and 43.4 Ω sq⁻¹ at 92.9% transmittance,



Fig. 7 (a) Transmittance of the hybrid films with a single layer and with five coatings of AgNW/PEDOT:PSS according to the sheet resistance. (b) Transmittance spectra of ITO film and hybrid films coated five times (0.28 wt% AgNW solution) AgNW/PEDOT:PSS.

respectively. The sheet resistance of multi-layer coated composite showed a decreased value by 50.9% compared with the single-layer coated composite at high transmittance. This indicates that multi-layered AgNW has enhanced optical properties, including its haziness. The optical transmittance over a large wavelength range is shown in Fig. 7b. The value includes the reflection of the PET substrate. The transmittances of multi-layer AgNW/PEDOT:PSS composite films with sheet resistance values of 58.6, 36.3 and 19.3 Ω sq⁻¹ were 87.1, 86.5 and 84.0% at 550 nm, respectively. The transmittances show a tendency to decrease slightly as the sheet resistance is reduced. Interestingly, in a comparison with ITO film, the transmittance of the multi-layer AgNW/ PEDOT:PSS composite film with a sheet resistance value of 58.6 Ω sq⁻¹ was 9.1% higher than that of an ITO film with a sheet resistance value of 55.2 Ω sg⁻¹. Also, the transmittance levels of not only the multi-layer AgNW/PEDOT:PSS composite films but also the ITO film deposited onto PET substrates were nearly constant over the visible light region.

AgNWs have excellent mechanical flexibility without a change in their conductivity due to the intrinsic flexibility of silver. In

contrast, traditional ITO film can crack when it is bent because ITO is a brittle ceramic material.^{37, 38} The change in the sheet resistance of the multi-layered AgNW/PEDOT:PSS composite film was examined as a function of the radius of curvature to determine the flexibility. In Fig. 8, the sheet resistance of the



Fig. 8 Bending test and comparison of the AgNW/ EDOT:PSS hybrid film and ITO PET film, showing a change in R/R_0 with an increased radius of curvature.

multi-layer AgNW/PEDOT:PSS composite film increased only by 1.2% at a radius of curvature of 1.5 mm. This change in the sheet resistance with a change of the radius of curvature may be due to a change in the geometrical slipping and delamination at the AgNW junctions.³⁹ In contrast, the ITO sheet resistance increased significantly to 41.9 % when a radius of curvature of 2.5 mm is reached. This result is consistent with reports of ITO cracking under a large degree of bending.

The patternability of transparent electrode is necessary and critical technique for optoelectronic devices such as organic light-emitting diodes (OLED) and touch screen panel applications which need desired circuits. In addition, visibility of pattern geometries is important for transparency, therefore small sized pattern is desired. The patterns with above 50 µm width are unsuitable for optoelectronic device applications because the pattern line with wider than 50 µm is clearly visible to the naked eye. As shown in Fig. 9, the AgNW/PEDOT:PSS hybrid films was successfully patterned with narrow widths below 50 µm using by photolithography and wet etching method. The AgNW/PEDOT:PSS was clearly etched by etchant which can dissolve the AgNWs and decompose PEDOT:PSS. The pattern with 30 µm width was successfully obtained as shown in Fig. 9c and the resistance of remained active area was maintained.

4. CONCLUSION

In conclusion, we developed an effective method to fabricate highly conductive and reliable AgNW/PEDOT:PSS hybrid composite films with an excellent optical transparency, enhanced haziness, and a low electrical deviation on large-area film. This is achieved by a multi-layer coating process of an AgNW solution and a thin over-coating layer of highly conductive PEDOT:PSS. The electrical standard deviation and optical transmittance of the AgNW/PEDOT:PSS composite films were found to depend on the number of AgNW coating cycles. A multi-step coating of diluted AgNWs formed wellarranged and well-organized AgNW conductive networks using



Fig. 9 Optical images of the patterned AgNW/PEDOT:PSS hybrid film by photolithography patterning process. (a) Removal of unexposed photoresist with developer solution. (b) Wet etching of the photoresist coated AgNW/PEDOT:PSS hybrid film. (c) Photoresist removed AgNW/PEDOT:PSS hybrid film with 30 μ m line width.

fewer AgNWs. The resulting film showed enhancements of its transparency, haziness, and reliability compared to a traditional one-pot coating of a single layer using a concentrated AgNW solution. In addition, the highly conductive PEDOT:PSS enhanced the electrical properties, including the percolation threshold, electrical standard deviation, and sheet resistance of the films. A film with a smoother surface could be obtained by the encapsulation of AgNWs with PEDOT:PSS, while the conductivity was reduced with an increase in the thickness of the PEDOT:PSS. The fabricated highly reliable AgNW/PEDOT:PSS films showed excellent electromechanical flexibility and good stability. In addition. the AgNW/PEDOT:PSS film was successfully patterned by photolithography and wet etching processes. The resulting patterns showed 30 µm width and stable resistance values. The patternability of hybrid conductive film can be used for transparent electrode with desired circuits. We believe that this technical approach will help with the development of metal nanomaterial-based transparent electrodes with good flexibility, high efficiency, reliability and high quality levels for optoelectronic devices.

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The multi-layer coated AgNW/PEDOT:PSS films showed the excellent electrical standard deviation and enhanced optical properties without any further process. Furthermore, introduction of PEDOT:PSS could reduce standard deviation to below 2.